Hydrogeological Characteristics of Hartbeespoort Dam

Aqeelah Davis

Student number: 747025

Supervised by Prof. T. Abiye

In partial fulfilment of the requirements for the degree of Masters of Science in Hydrogeology

WITS UNIVERSITY

School of Geosciences

University of the Witwatersrand

May 2017

Declaration of Plagiarism

I _____ (Student number: _____) am a student registered for the degree of _____ in the academic year _____.

I hereby declare the following:

- I am aware that plagiarism (the use of someone else's work without their permission and/or without acknowledging the original source) is wrong.

- I confirm that the work submitted for assessment for the above degree is my own unaided work except where I have explicitly indicated otherwise.

- I have followed the required conventions in referencing the thoughts and ideas of others.

- I understand that the University of the Witwatersrand may take disciplinary action against me if there is a belief that this is not my own unaided work or that I have failed to acknowledge the source of the ideas or words in my writing.

Signature: _____ Date: _____

Acknowledgements

This research was conducted as a part of the GRECHLIM project (PEER) and I would like to thank the School of Geosciences at the University of the Witwatersrand (Wits) and International Water Management Institute (IMWI) for the support provided.

Many thanks to Dr. Karen Villholth for her support during the groundwater recharge training. Thank you to the Department of Water and Sanitation (DWS) for the abundance of help with information and to Mr Mike Butler from iThemba Laboratory in Gauteng who supplied me with the high quality laboratory work done on the tritium isotopes.

I would like to thank my Supervisor, Professor T. Abiye for the time and support he has given me throughout the process as well as his laboratory work done on the stable isotopes at the University of Witwatersrand.

Thank you to my peers, Khahliso Leketa, Silindile Zondi, Chelsea Rebelo and Khuliso Masindi who played a supportive role in encouraging me to do my best:

Thank you to my family and partner for encouraging me to pursue my higher education.

Abstract

Hartbeespoort Dam, the source of irrigation and potable water for the local community of Hartbeespoort area is a vulnerable water resource. The aim of this research was to evaluate the interaction between dam water and groundwater as well as characterise the hydrochemical data from metals and tritium. The former was done through the application of environmental isotopes and the implementation of a long term water balance, while the latter used hydrochemical data to define the spatial distribution of metals and tritium.

The results indicated that the dam water is separated from the groundwater in winter. Two sources of mixing were recognized to have occurred downstream of the dam in 2015 but not in the Hartbeespoort dam area. These were identified as artificial through the runoff of agricultural water that was abstracted from the dam and through the pumping of water near the fault.

Higher than normal tritium concentration indicated that contamination comes through the Crocodile River after the fault connecting the river to Pelindaba, the nuclear power generation plant south of Hartbeespoort Dam in the Broederstroom area. The Crocodile River showed that the contamination of water by lead, 22.11ppb in summer and 3.8 ppb in winter, and cadmium,2.2 ppb in winter. The Magalies River feeds the dam with copper. All metals accumulate at the dam wall and settles in the sediment, diluting the downstream water. Boreholes near the dam and spring along the fault are vulnerable to contamination.

The water balance estimation resulted 18 345 472m^3, with a 3.9% error, gain of water to the dam from the groundwater greater than the amount exiting the dam to through groundwater. The groundwater entering the dam is estimated to be 32 517 704m^3. The groundwater exiting the dam is estimated at 14 172 232m^3. The difference in groundwater showed a decrease of 10 000 000m^3 over the 15 year period from 1st October 2000 until the 30th September 2015. Consequently, these results show an increased stress placed on the groundwater presumably due to an increase in groundwater abstraction from agriculture and the expanding mining area.

Table of Contents

List of Tables

List of Figures

Abbreviations

Bq/L	Becquerel per Litre
Cu	Copper
Cd	Cadmium
DO	Dissolved Oxygen
DWA	Department of Water Affairs
EC	Electrical Conductivity
GMWL	Global Meteoric Water Line
PLMWL	Pretoria Local Meteoric Water Line
TDS	Total Dissolved Solids
T.U.	Tritium Units

Chapter 1: Introduction

1.1 Background

1.1.1 Historical

In 1923, the Hartbeespoort Dam was built as an impoundment for the surrounding area to irrigate farm land and supply the local community with potable water (Harding, 2004; Venter, 2004). Located at 25°44′51″S and 27°52′1″E, as seen in Figure 1, between the city of Pretoria and the mining town of Rustenburg the dam is a landmark on the eastern border of the North West Province in South Africa. The area has been historically surrounded by mines and farmlands. Since 1923, the booming mining industry has given rise to the expansion of mining towns and also the expansion of cities such as Johannesburg and Pretoria (Harding, 2004; Venter, 2004). Over time this has also increased the growth in population and thus demand on water for further use in agriculture and an increased number of boreholes for private homes (Ashton et al., 1985). The increased population has also increased the amount of sewage entering the dam and thus the influx of contaminants has increased (Ashton et al., 1985; DH Environmentals, 2004; Harding, 2004; Venter, 2004). These days the dam is used for more than just a natural resource but also as a tourist attraction for recreational purposes (Harding, 2004; Venter, 2004). Thus when problems such as poor odour, algae, desertification of plants and animals and health issues such as rashes and gastroenteritis were identified in Hartbeespoort Dam, a remediation initiative was introduced (Thornton et al. 1989). Nutrient influx from the rivers has increased such problems as algal blooms and accelerated rates of eutrophication (Toerien & Walmsley, 1978; Harding, 2004; Venter, 2004). The upstream presence of industry has also added to pollutants, such as heavy metals, entering the dam which causes health issues for flora and fauna (Wittmann & Forstner, 1975; Abiye et al., 2015). Other more discrete contaminants, such as radionuclides and harmful bacteria, have been discovered in the dam but as of yet have not been explored as a source of contamination (Ginkel, Hohls & Vermaak, 2001; Abiye et al., 2015).

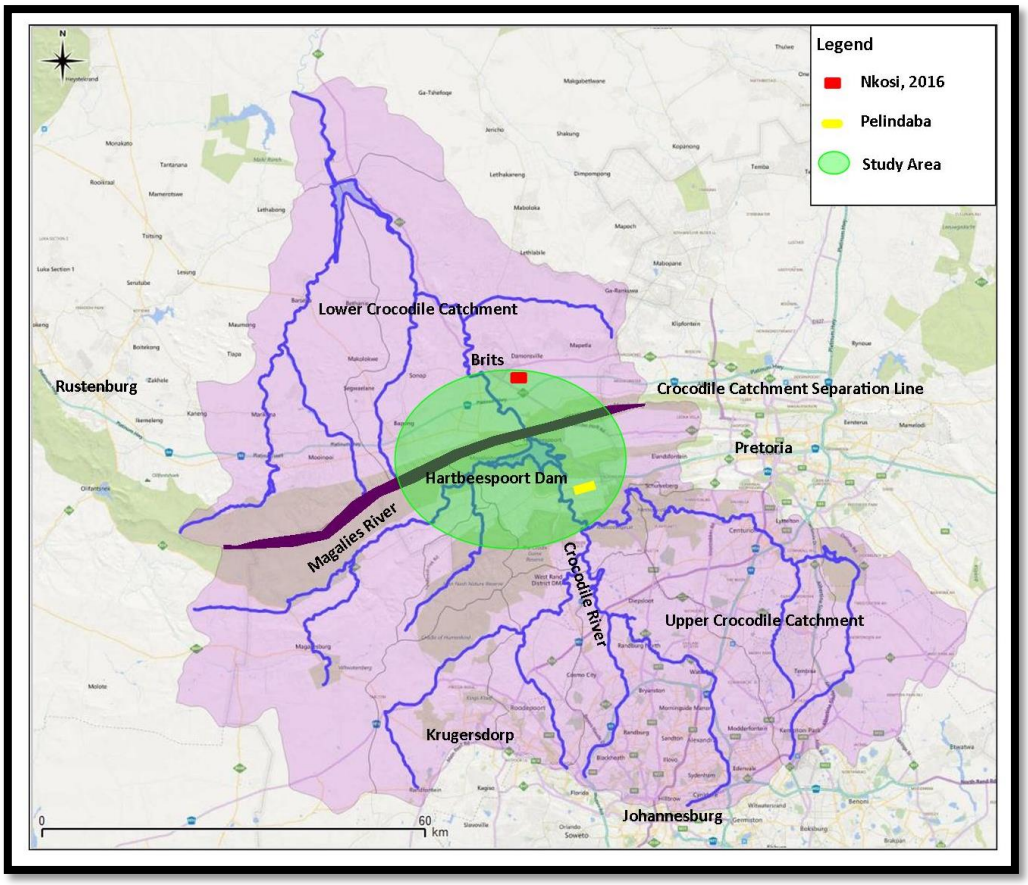

Figure 1: The Hartbeespoort Dam study area location within the Upper Crocodile catchment as well as Nkosi, 2016 study area.

1.1.2 Study Area

Hartbeespoort Dam and the surrounding area is the primary focus of this study. It is surrounded by the Magaliesburg quartzite mountains, which created a valley and lake microclimate. It is a mixed land use area with recreational, industrial, agricultural and residential activities. Most of the areas around the edges of the dam, are privately owned businesses and residences which make sampling surface water difficult. Boreholes are also privately owned and are difficult to access.

1.1.3 Climate

The local climate of Hartbeespoort Dam has a wet and a dry season (Figure 2). Like the majority of South Africa warm, rainy summer months occur from October to March, while cold, dry winters occur the rest of the year (DWA, 2009). This semi-arid region has an average of between 559-678 mm/yr of rainfall, which is contributed by a combination of orographic and microclimate as a result of the dam as well as regional thunderstorms (DWA, 2009). The dominant wind direction is from the north east while average temperatures in summer are a minimum of 15℃ and a maximum of 30° C while winter temperatures are 5° C in the evening and 24℃ at midday as in Figure 3 (DWA, 2009; SaExplore, 2014).

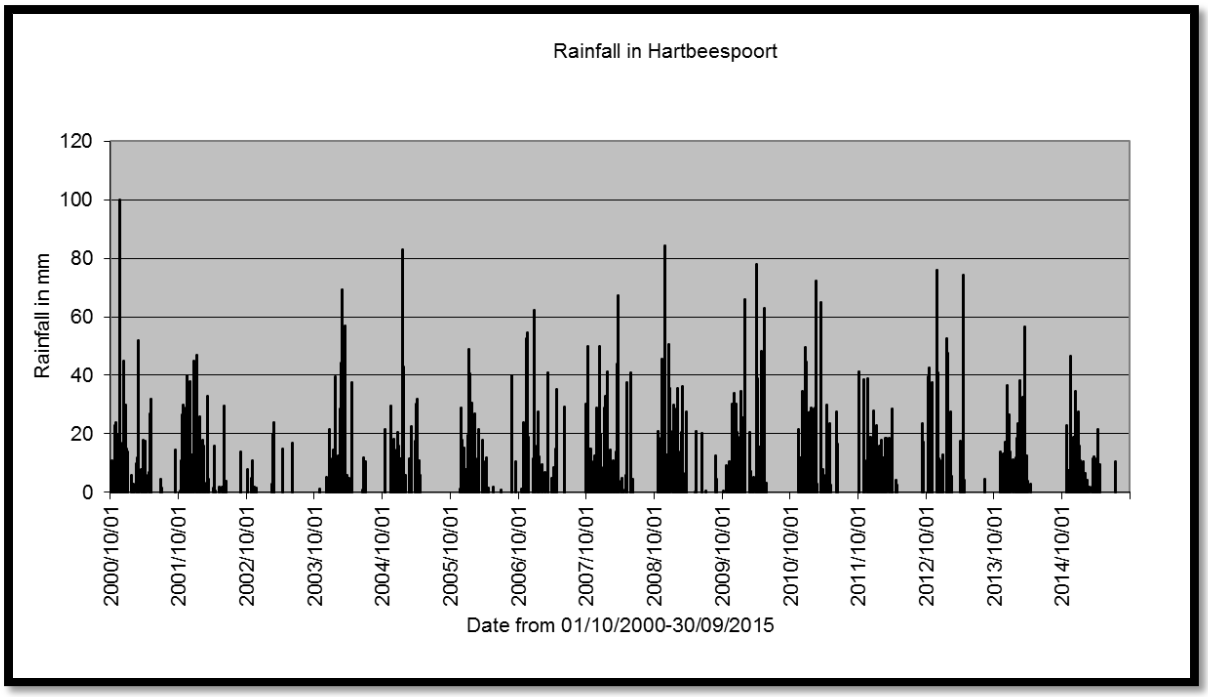

Figure 2: Long term rainfall data for Hartbeespoort area from 01/10/2000 to 30/09/2015 showing the rainfall variability and decrease in maximum rainfall over time.

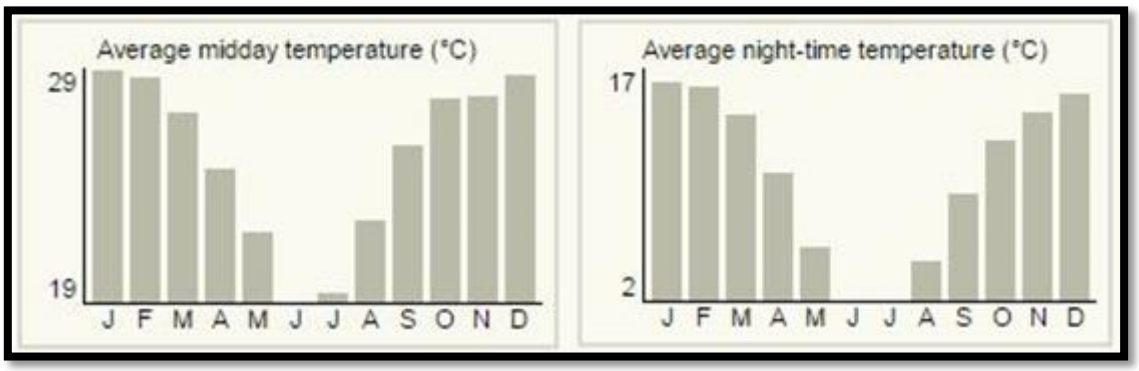

Figure 3: Average yearly midday and night time temperatures for Hartbeespoort (SaExplore, 2014).

1.1.4 Geology and Hydrology

The general geology of the Hartbeespoort area consists of the Chuniespoort group, overlain unconformable by the Pretoria Group and intruded by the Bushveld Complex. The rocks are karstic dolomites which were deposited between 2 643 and 2 520 million years ago (Leyland, 2008).

The hiatus between the Chuniespoort Group and the Pretoria Group is approximately 80 million years represented by an erosional unconformity (Leyland, 2008). The Pretoria Group

consists of fractured quartzites, shales and extrusive andesites which are 2 350 to 2 100 million years old (McCarthy & Rubridge, 2005).

The Bushveld Complex postdates the Pretoria Group as it intruded at 2 061 million years ago (McCarthy & Rubridge, 2005). This consists of the interlayering of norites, anorthosites, pyroxenites and chromatites with the intrusion of Lebowa Granites. The Bushveld Complex intrusion caused the subsequent folding of the Transvaal Supergroup to dip 20˚ towards the centre of the intrusion (Cheney & Twist, 1991; Cawthorn & Webb, 2001; Leyland, 2008). The Bushveld Complex also caused dykes and sills to intrude the Pretoria Group, and metamorphosed the Chunniespoort and Pretoria group (McCarthy & Rubridge, 2005; Leyland, 2008; Nkosi, 2016). This geology was shown in Figure 4 where the younging direction is towards the southeast.

The geology in the Hartbeespoort Dam area consists of the Pretoria group, which forms part of the larger Transvaal Supergroup (Leyland, 2008). The lithology includes interbedded quartzites and shales with igneous intrusion of andesites (McCarthy & Rubridge, 2005; Leyland, 2008). The quartzite and shale layers strike northeast-southwest with a northwest younging direction (Leyland, 2008). The quartzites, which are more resistant to weathering, make up the ridges, and the easily-weathered shales and andesites, gave rise to the valleys in Hartbeespoort (McCarthy & Rubridge, 2005). There are two steeply dipping, northwest-southeast trending normal faults that cut the dam site, creating a graben (Eales & Cawthorn, 1996). These faults crosscut the 20˚dipping, shallow northwest dipping quartzite strata. The underlying geology of the dam is said to be monomictic, underlain by quartzites, which are fractured and faulted, but diabase and shales also crosscut the faults with intruding norite and granites (Cheney & Twist, 1991; Cawthorn & Webb, 2001; Leyland, 2008). The underlying rocks consist of the Chuniespoort dolomites (McCarthy & Rubridge, 2005).

In Eales and Cawthorn (1996), the Western Limb of the Bushveld Complex and underlying Transvaal Supergroup show the extent of the Brits Graben (Eales & Cawthorn, 1996). The faults are steeply dipping SSE-NNW striking normal faults which created a graben with a displacement of 600m (Dube, 2010). This crosscut the Bushveld Complex and thus postdates it (Dube, 2010). The lithology of the Pretoria Group quartzites at the Hartbeespoort dam wall are dipping at 20˚N and striking SW-NE (Cheney & Twist, 1991). This strata is crosscut by two steeply dipping faults dipping to the NEE and SWW which forced the central block to

move down and horizontally displace to the SSE by 600m (Cheney & Twist, 1991; Eales & Cawthorn, 1996; Dube, 2010).

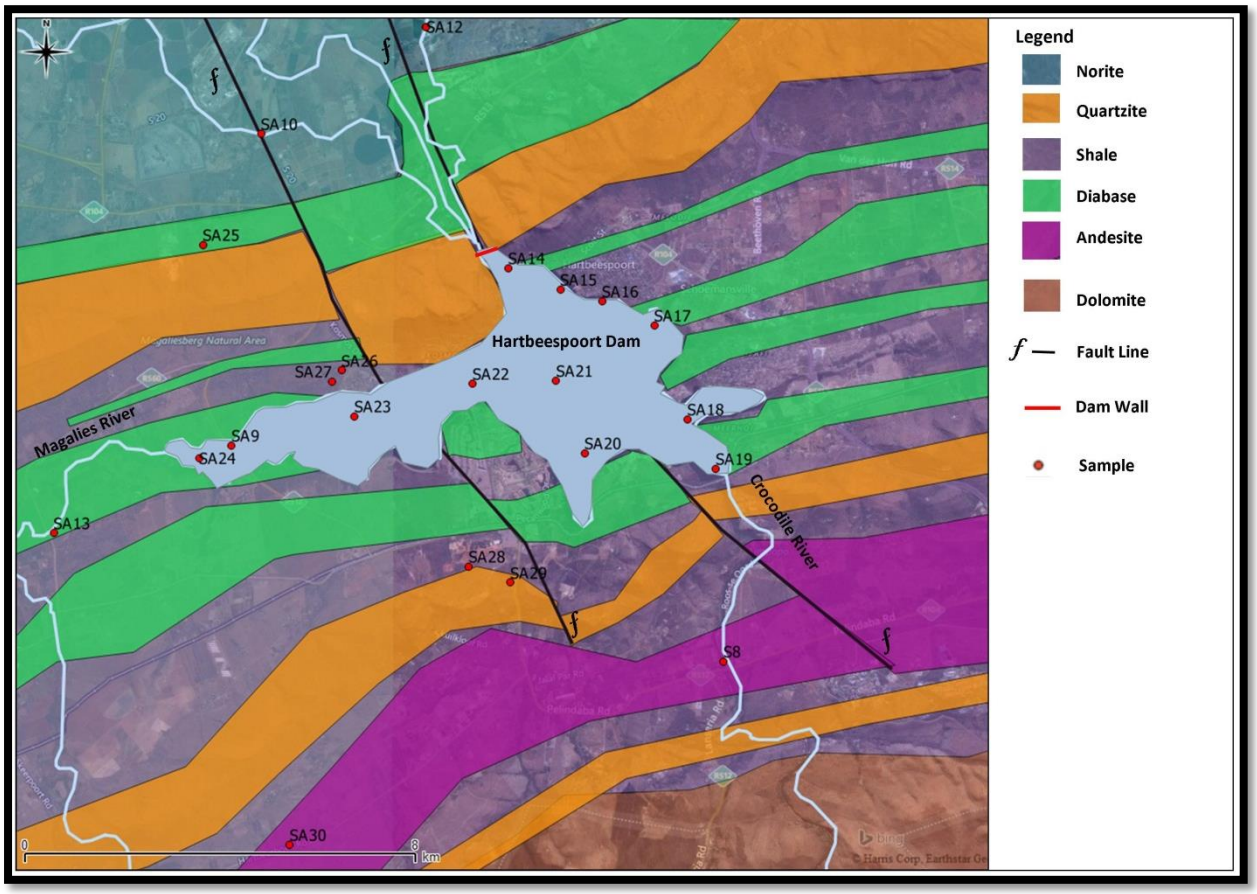

Figure 4: Geological map of the study area illustrating the importance of the geology and structures on the hydrogeology and the possible contamination of Hartbeespoort Dam adapted from a Department of Mines and Industry map sheet 1 of Pretoria (Union of South Africa).

Hartbeespoort dam is a hypertrophic dam that forms the northern most part of the Upper crocodile catchment, as seen in figure 1, and is fed by a catchment area of 4144km^2 (Chutter & Rossouw, 1991). The Magalies River, Crocodile River, Leeuspruit and Swartspruit, which flow from Krugersdorp, Johannesburg and Pretoria, drain their waters into the Hartbeespoort Dam (Chutter & Rossouw, 1991).

The trend for over a decade, from 1980 to 1990, was for treated effluents, entering the dam, to increase from 69 000 000m^3 to 105 000 000m^3 (DWA, 2009). This has added to the nutrient loading experienced in the dam. In 2008 effluent loads reached 715 400 000m^3 of

sewage (Roux & Oelofse, 2010), this would need to be considered as a factor when separating groundwater from surface water in the rivers entering the dam.

1.2 Problem Statement and Hypothesis

A water balance of the reservoir has not yet been attempted in order to assess the hydrological components and the role of groundwater in controlling the concentration of contaminants in the water. Without some treatment, the concentration of contaminants can make the water unfit for human consumption, as well as for irrigational use. Leakage from the dam wall should be assessed as this also affects the results of the water balance.

Groundwater is the direct source of drinking water for most people in an arid or semi-arid country which relies on wells and boreholes for water during periods of water shortages (Braune & Xu, 2009). Contamination of both groundwater as well as surface water by heavy metals can pose a health risk to consumers. This contamination can be either from anthropogenic input or by water-rock interaction (Bradl, 2005). Hartbeespoort Dam has been monitored over the years for heavy metal content but mapping of contaminants in the water over the entire surface area has not been attempted. Furthermore despite groundwater and surface water interaction being studied in the Upper Crocodile catchment, using environmental isotopes, the Hartbeespoort Dam does not obey the mixing line (Abiye et al., 2015). If the surface and ground water samples are compared by environmental isotopes, will they show mixing or separation and what effect would this have on the heavy metal pollution?

Tritium can be found in low concentration in the atmosphere of the Southern Hemisphere compared to that of the Northern Hemisphere and contaminated areas(Abiye et al., 2015). The mean local rain value is about 5.6 TU. Hartbeespoort Dam shows considerably higher values averaging 12.6 TU around the edges (Abiye et al., 2015). This indicates contamination from anthropogenic sources (Abiye et al., 2015). This can occur by the generation of nuclear power and subsequent removal of waste, bomb testing and leakage from underground nuclear waste storage. The interior of the dam has yet to be characterized and the source has yet to be assessed as a constant input or a series of sporadic injections (Abiye et al., 2015). 12.6 TU, as seen from the dam rim samples, is the equivalent of 1.49 Bq/L which is greater than the drinking water standard of the World Health Organization of 0.5 Bq/L, and that of the Department of Water Affairs in South Africa, which is 1.38Bq/L. The pattern of

concentration from Abiye, et. al.'s, (2015) data indicates that the source is most likely from the south eastern rivers just north of the Malmani dolomites which necessitate confirmation.

1.3 Aims and Objectives

The aims of this research project are as follows:

1. To identify the Hartbeespoort Dam and groundwater relationship through an environmental isotope approach (^{18}O, ^{2}H and ^{3}H) and water balance method.
2. To spatially map metal and tritium distribution in the dam and identify the influence of dam water on the surrounding groundwater.
3. To use the baseflow separation method to calculate the baseflow of the rivers entering the dam as groundwater inflow.
4. To measure the water exiting the dam through the ground.

Chapter 2: Literature Review

2.1 Hydrogeology

2.1.1 Water Balance Models

A water balance is defined as a numerical method of expressing the volume change of water with respect to hydrological processes (European Commission, 2015). This method takes into account the water entering and exiting the desired observed system (European Commission, 2015). The method uses the law of mass conservation which states that, at dynamic equilibrium, the change in mass, over time, should be the difference between input and output factors of a closed system (Vorster, 1985; Moriarty et al., 2007). The continuity of the hydrological cycle allows for this method to be represented numerically (European Commission, 2015).

The procedure for applying a water balance method to an area is to firstly establish a temporal and spatial boundary and then to assess the unknowns of interest in the area that need evaluating (Moriarty et al., 2007). Furthermore a schematic model should be created to establish a visual representation of the particular system under observation (Moriarty et al., 2007). Then sources of time relevant quality data should be identified and used (Moriarty et al., 2007). Missing data should be generated using quality controlled estimates in order to produce a water balance that provides useful information for policy makers (Moriarty et al., 2007).

There are several uses for this hydrological method which helps policy makers to formulate informed decisions about the availability of water and how to manage this resource in a sustainable manner (Moriarty et al., 2007; European Commission, 2015). The water balance can indicate stresses on the water system such as increased demand in times of drought (Moriarty et al., 2007; Vining & Vecchia 2007; European Commission, 2015). Policy makers use the information gathered from a water balance to set suitable extraction rates with respect to the rate of recharge (European Commission, 2015). It can also asses the long term groundwater available in the system (Vining & Vecchia 2007; European Commission, 2015).

A water balance approach can also elucidate the type of transport of substances within the water system (European Commission, 2015). The type of transport can either concentrate or diffuse the risk of pollutants or contaminants in the groundwater making the results of a water

balance, in certain instances, vital to understanding the pathways and possible sumps associated with it (European Commission, 2015).

Water balances are by no means perfect and uncertainty can occur from many temporal and spatial inconsistencies, as well as measurement errors (Moriarty et al., 2007). To eliminate these uncertainties data should be quality controlled and temporal and spatial boundaries should be demarcated (Moriarty et al., 2007). To assess uncertainty, a good holistic understanding of the area of interest should be known (Moriarty et al., 2007).

In the Hartbeespoort Dam a hydrological reservoir water balance was conducted in 1985 to assess the storage of water available for the use as potable and irrigation water (Ashton et al., 1985). The temporal extent of the study was taken over a period from 1964-1978 (Ashton et al., 1985). The study did not take into account the effect groundwater had on the system and thus left room for improvement on the water balance method.

A lake system can either be connected or disconnected to the groundwater table. Rock type can be a determining factor in assessing this losing or gaining system. In the Brunner et al. (2009), a theorized model was proposed using an idealized circular lake disconnected from an isotropic and homogeneous aquifer. Brunner et al. (2009) also found that it is more likely for lakes to be disconnected than a river. Hartbeespoort dam shares these traits as well as being situated in a semi-arid area and as such will be assumed to be a disconnected system due to thick crystalline rock underlying the dam. In order to confirm this, further study with piezometric maps should be conducted.

The water balance method can be represented by the simple formula of (Moriarty et al., 2007)

:

$$P=Q+E\pm\Delta S \qquad (1)$$

Where P is precipitation, Q is run-off, E is evaporation and ΔS represents the change in storage of either a dam, aquifer or soil (Moriarty et al., 2007). This only considers the surface processes and does not take into account the groundwater system.

A study on the Williams Lake in Minnesota looked into the groundwater seepage of the lake (Labaugh et al., 1997). The study used a combination of a flow net approach and water budget with chemicals and isotopes to determine the change in storage (Labaugh et al., 1997). The water budget equation used in this study is as follows (Labaugh et al., 1997):

$$\Delta V = P + GWI - E - GWO \quad (2)$$

Where

ΔV	Change in storage
P	Precipitation
GWI	Groundwater input
E	Evaporation
GWO	Groundwater output

Similarly a water balance study by Kumambala and Ervine (2010) for the Lake Malawi was conducted to ascertain the storage in the lake over time. The study also forward-modelled change in storage by incorporating climate change data to determine if water shortages and overflowing would occur in the future (Kumambala & Ervine, 2010). This factor affected rainfall and evaporation but had no large impact on future water levels in Lake Malawi (Kumambala & Ervine, 2010).

In the Reta (2011), Modflow was used to model the water balance of Lake Naivasha in Kenya, one of the country's important sources of fresh water. The lake was being utilized for agriculture to improve production and industrial development in the area (Reta, 2011). The water balance was applied to evaluate the groundwater supply as a resource and subsequent storage in the lake for sustainable use (Reta, 2011).

In the case of the Hartbeespoort Dam, a simple water balance approach was adopted and applied with net flux since no data was available for isotopic or chemical concentrations of evaporation. It will only give the difference between the groundwater going in and out of the dam. The formula calculates the change in groundwater to show the dam as either a gaining or losing system. The model of the change in groundwater assumes sewage inflow is equal to sewage outflow from the dam. The influx of waste water into Hartbeespoort Dam is an anthropogenic component of the discharge entering the dam and as such will be inclusive in the river input. The amount of waste water should be subtracted from the discharge in order to get the natural base flow and rate of run-off entering the system.

A model of the groundwater interaction was created as seen in Figure 5 for the purpose of a baseflow calculation.

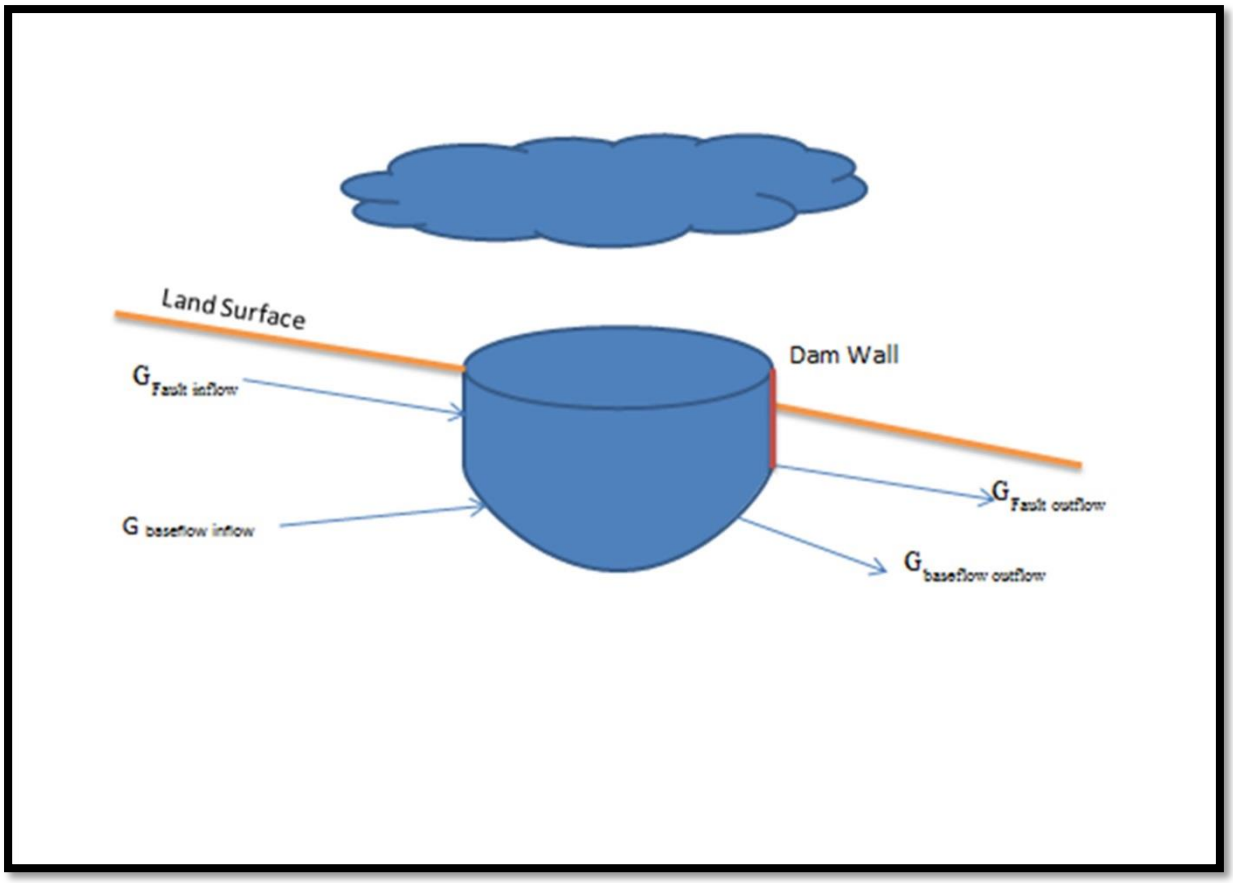

Figure 1: The model of groundwater interaction to determine a suitable equation to calculate the baseflow exiting the dam.

This can be represented by the formula:

$$\Delta G = G_{inflow} - G_{outflow} \text{ in m}^3 \qquad (3)$$

Where

ΔG is the difference in groundwater inflow and outflow from the dam

G_{inflow} is the total amount of water entering the dam from the groundwater

$G_{outflow}$ is the total amount of water exiting the dam to the groundwater

The formula can be further manipulated so that the amount of groundwater exiting the dam can be calculated and represented thusly:

$$G_{outflow} = G_{inflow} - \Delta G$$

If groundwater from the fault is assumed to be the same coming in as it is going out then the total groundwater leaving the dam can be calculated excluding that of the fault.

To calculate baseflow, the baseflow separation method can be used. The description of a hydrograph analysis, as given by Vegter and Pitman (2003), is the separation of the hydrograph into two portions; the runoff and the baseflow. Runoff includes all surface water and interflow while the baseflow is the groundwater component (Bean et al., 2003). The method takes the measured flow in equal increments of time and separates the baseflow from the quickflow (Bean et al., 2003). The method uses the formula (Bean et al. 2003):

$Q_i = QG_i + QS_i$ in m^3 (4)

Where

Q_i is the total flow

QG_i is the incoming groundwater

QS_i is the surface runoff entering the weir

Although monthly values were used to calculate the amount of groundwater and runoff, daily values are more accurate as seen in Hughes et al. (2003). The separation algorithm is represented by equation 5(Hughes et al. 2003):

$$q_i = \alpha q_{i-1} + \beta(1 + \alpha)(Q_i - Q_{i-1}) \quad (5)$$

Where:

Qi = total flow time series

qi = high-flow time series component

QBi = baseflow time series component

i = time step index

α, β = separation parameters ($0<\alpha<1$, $0<\beta<0.5$)

The values used for α and β were fixed at 0.995 and 0.5 for South Africa due to its effectiveness after many iterations done by Smakhtin and Watkins (1997) and assessed as being ideal for the area. The fixing of β was acceptable for monthly data and the α parameter would settle to an acceptable value (Hughes et al., 2003). This was a double parameter baseflow separation method. For the Hartbeespoort Dam sample calculations, a single parameter recursive digital filter method which uses attenuation of α fixed at 0.995 will be

used for long term daily discharge data of the Magalies River and Crocodile River weirs just before the dam. Where α filters off the high peaks and leaves a baseflow. This will represent the baseflow of the river plus the sewage. Thus the sewage will need to be subtracted from this value to get the true baseflow. The use of information provided by the Department of Water and Sanitation will be used to subtract abstraction from the value calculated.

2.1.2 Surface Groundwater Interaction

Hartbeespoort Dam has been studied by environmental companies and the Department of Water and Sanitation in a less holistic method. It did not consider that surface water, groundwater and geology are dynamically interacting components of the earth system. The environmental isotopic signatures of groundwater and surface water can help to identify mixing as well as sources of water (West et al., 2014). The use of the isotopes in conjunction with the water balance assesses whether the system is connected or disconnected, thus losing or gaining water. It also assesses whether it is from mixed sources.

The use of environmental isotopes showed the presence of extensive interaction of surface and ground water in the Upper Crocodile Catchment (Abiye et al., 2015). The dam samples did not follow this trend (Abiye et al., 2015). The samples around the dam were surficial and only taken at the edges of the dam and so they could not be compared with groundwater in the area (Abiye et al., 2015).

Nkosi (2016) applied stable isotopes of ^{18}O and ^{2}H and tritium to characterize an area northeast of Hartbeespoort dam The samples from both aquifers plotted in the same cluster and thus indicated mixing between both aquifers (Nkosi, 2016).

Table 1: Nkosi, 2016 stable isotope data with locations.

Monitoring Point	Longitude	Latitude	Tritium (T.U.)	$\delta^{2}H$‰	$\delta^{2}H$ StDev	$\delta^{18}O$‰	$\delta^{18}O$ StDev
BH-B1	27.8419	-25.6629	5.7	-6.9	0.22	-1.17	0.04
PW-DAM	27.8361	-25.6603	7.3	-2.75	0.06	-0.8	0.05
BH-SM1	27.8395	-25.6628	5.3	5.83	0.11	1.28	0.04
BH-SM2	27.8398	-25.663	6.9	9.98	0.13	2.15	0.04
BH-PM1	27.8366	-25.6669	3.5	-19.6	0.09	-3.49	0.07
BH-PM4	27.8319	-25.6615	4.4	-15.09	0.19	-2.83	0.04
BH-PM5	27.8333	-25.6623	4.6	-3.93	0.17	-0.64	0.03
BH-PIM1	27.8311	-25.6649	7.1	-7.54	0.22	-0.79	0.01
BH-PIM4	27.8369	-25.6664	6.4	-1.81	0.16	-0.54	0.03

The normal faults in the Hartbeespoort area, which created the Brits Graben, should act as hydraulic barriers and should also act as a hydraulic conduit which draws water to greater depths in the dam (Nkosi, 2016).

2.1.3 Geological Structure Interaction

Faults can either transport or become barriers for water flow. For normal faults the former is true but with reverse and strike-slip faults water is barred from passing through. The Hartbeespoort Dam is built on the Brits Graben, as seen in figures 3, 6 and 7, which consists of not only normal fault displacements but also horizontal displacement of approximately 600m south (Eales & Cawthorn, 1996; Dube 2010).

Figure 2: Image from the top of the Hartbeespoort cable cart illustrating the displacement south of the Magaliesburg quartzite ridge, at the Hartbeespoort Dam wall, by the Brits Graben.

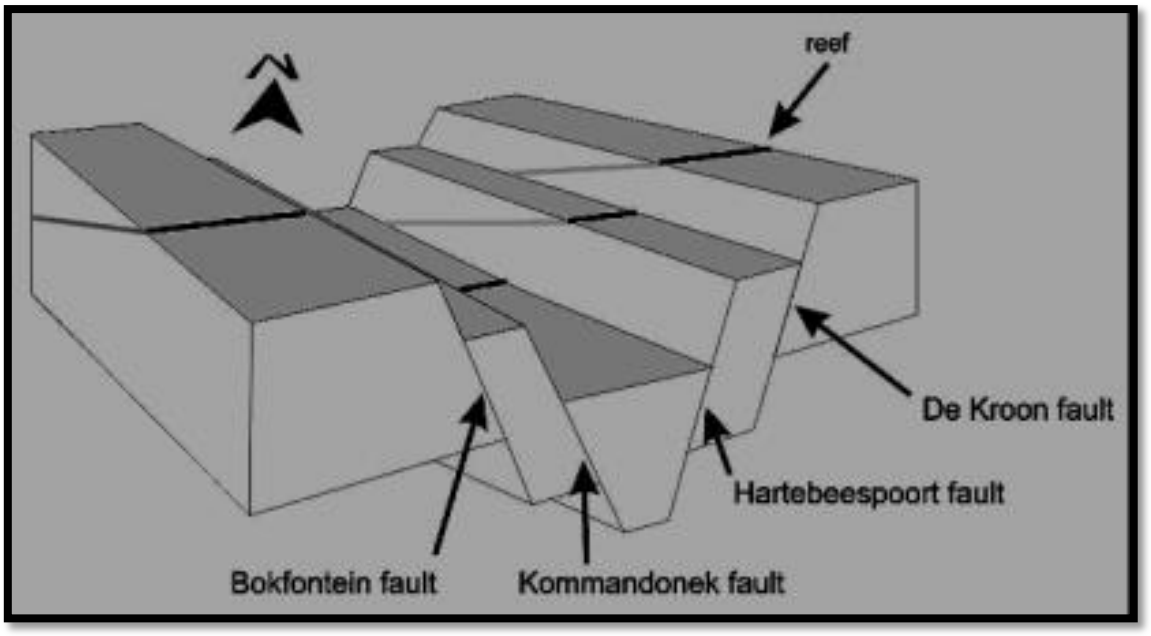

Figure 3: Schematic of the Brits Graben further north of the Hartbeespoort Dam (Eales & Cawthorn, 1996).

At the dam wall, the Crocodile River runs along the Hartbeespoort Fault (Eales & Cawthorn, 1996). The faults pose a possible seepage point for water from the Hartbeespoort Dam, which affects surface water leaving the dam and is a conduit for groundwater to enter the dam. The Brits Graben in the Hartbeespoort area is not well studied. However, the area and structure to the north where the Bushveld Complex lays, is better understood.

The shift in elevation of the Brits Graben as well as the horizontal displacement was observed and the horizontal displacement is approximately 600m while the vertical displacement is approximately 50m (Nkosi 2016).

2.2 Metals

2.2.1 Dam Chemistry and Metals

Hartbeespoort Dam was described as a hypertrophic dam which overturns in April of each year Robarts et al. (1982), This means that Hartbeespoort Dam is significantly warmer with mixing of temperature and dissolved oxygen occurring in April (Robarts et al., 1982).

In a study by Ashton et al. (1985) on Hartbeespoort Dam, the pH measurement from 1980 to 1984 taken in the eplimnion ranged from a maximum of 10 to a minimum of 8.3. This showed that the water in the dam is alkaline (Ashton et al., 1985). In a more recent study by Abiye et.al. (2015),samples collected from the dam edges from 2008-2012 showed an average pH value of 9.1, which is similar values gained from the study conducted in 1985

(Ashton et al. 1985). This alkaline water has a pH value higher than 8.4, which is the cut off limit without treatment as defined by the Department of Water Affairs, and would cause problems for the farmers that irrigate their crops with the Hartbeespoort Dam water (DWA, 1996b). This would increase the solubility index of the water and the possibility of metals forming as salts in the soil when used for crop irrigation (DWA, 1996b).

2.2.2 Metal Indicators

Wittmann and Forstner (1975) used sediment as an indicator of heavy metal pollution. They go on to say that in general, away from the sea, there are five main sources of pollution. These include weathering of rocks, leaching of waste, sewage and manure, processing plants and the use of metals and their compounds (Wittmann & Forstner, 1975). In their work, samples were taken over a variety of depths and for a variety of metals which covered the entire dam area. The Pb and Cd were highest in the sediment, coming from the Crocodile River and the highest Cu was coming from the Magalies River (Wittmann & Forstner, 1975).

According to Coetzee (1993) the sediment in the Hartbeespoort Dam was tested for 10 metals and evaluated for remobilization risks. This study showed that a large proportion of metals were geochemical in origin and from the Transvaal Complex (Coetzee, 1993).

Fish have been studied as an indicator of metal pollution in the dam as they are resilient to pollution (Botha, 2012). The study showed that metal pollution in the Hartbeespoort dam was negatively affecting the fish reproduction and thus population in the dam (Botha, 2012). This indicates that not just the sediment contains metals but there are suspended metals in the water affecting the aquatic fauna (Botha, 2012).

In a case of study by Berg et al. (1995) conducted on Lake Kariba in Zimbabwe, it was discussed that metals found in fish were a good indicator for metal pollution in water and not sediment but liberated metals. Metal ions in the water will be tested and mapped in this study due to the indications from Botha's (2012) study.

2.3 Tritium

2.3.1 Tritium in Surface Water

Tritium is a radionuclide and has a half-life of 12.46 years. It is used in hydrogeology as an age tracer for residence times within the last 50 years. Tritium is created in the atmosphere by neutron bombardment of nitrogen. Tritium emits β radiation and thus can have carcinogenic

effects when absorbed by the body through water and produce. (Geyh, 2000 ; Phillips & Castro, 2014)

Radioactivity has as yet not been considered as a contaminant in the Hartbeespoort dam area. Although, in Abiye etal. (2015), tritium was used to show mixing between the surface and the ground water of the Upper Crocodile River catchment, where anthropogenic source was accounted for high tritium value in the dam water. The values found in the dam were on average 12.6T.U. equivalent to1.48Bq/L and were only from surface samples taken from the edges of the dam (Abiye et al., 2015). With the current tritium value of rainfall of 5.6T.U. the dam water signals the impact of radioactivity.

In Nkosi (2016) the tritium content in groundwater samples ranges of 3.5-7.3 T.U. which indicated the recharge of recycled dam water. Since this was downstream of the Hartbeespoort dam there is already an indication of possible groundwater contamination at the dam. Tritium samples will be taken from both surface and groundwater samples to indicate sources and possible entry points. The initial natural tritium activity given by Abiye et al. (2015) is 5.6 T.U. Any sample value above this value shall be considered contaminated by anthropogenic sources.

Age determination using the nuclear decay equation for the half-life of tritium will be used as a source to distinguish between contaminated and uncontaminated samples. The value for h will be fixed at 12.46 years as stipulated in Jenks et al. (1950) and the initial activity will be fixed as 5.6 T.U. which is the average value for rain in Abiye et al. (2015). Negative values will be used as a quality assessment to confirm contaminated samples.

Chapter 3 Methodology

3.1 Sampling Points and Period

A preliminary assessment of the area was conducted in the rainy season. This assessment fed into a strategy for acquiring sample points. The first sampling period was on 6th March 2016 when the weather was clear after heavy rain the previous few days. Difficulties with access led to only five samples taken during the campaign. Three of these samples were from surface water, one from a borehole and the last from a tap drawing borehole water. All samples were tested for metals, $\delta^{18}O$, $\delta^{2}H$, ^{3}H, EC, TDS, pH and temperature. The positions of the first sampling areas are shown in table 2 and figure 8.

Table 2: GPS coordinates in decimal degrees of the March samples.

Sample Name	Latitude	Longitude	Type of Sample
S8	-25.7949	27.89435	Crocodile Input
SA9	-25.7592	27.80381	Dam
SA10	-25.7075	27.80922	Borehole
SA11	-25.6899	27.83967	Crocodile Output
SA12	-25.6899	27.83967	Tap

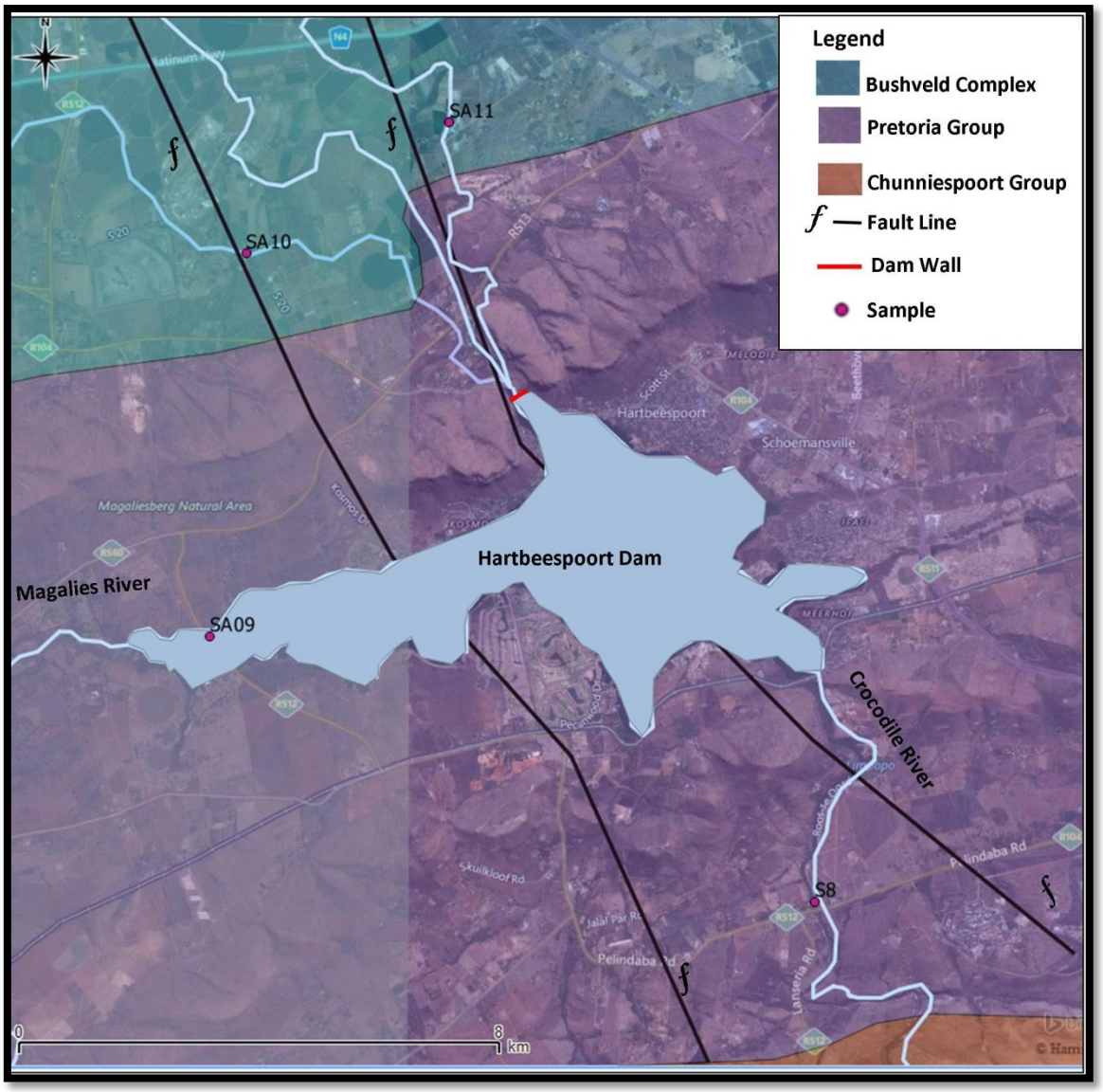

Figure 4: Sampling positions taken in March. The position of SA11 and SA12 are in the same area.

A second sampling period was planned for the dry months. Twenty-two samples were collected on the 4th and 5th June in 2016. All the samples were tested for metals, Environmental isotopes, DO, EC, TDS, pH and temperature.

A pre-planned traverse on the dam in a rented speed boat, using a GPS for navigation, was undertaken for sampling. Samples were taken using a bucket at 0.5m depths to avoid unrepresentative values.

The path chosen for sampling was based on bathometry and on the inlets and outlets of the rivers. The planned route across the dam had to be adjusted due to thick algal mats and water hyacinths blocking the way. 12 samples were gathered in just over an hour.

The water had no smell and was dark in colour so the bottom of the dam was not visible. Four borehole samples, one spring sample and one surface sample were taken in the afternoon.

These were tested for heavy metals, ^{3}H, $\delta^{18}O$ and $\delta^{2}H$, DO, EC, TDS, pH and temperature. All sample positions for June are recorded in table 3 and figure 9.

Table 3: Sample positions for the dry season.

Sample Name	Latitude	Longitude	Type of Sample
S8	-25.79494	27.89435	Crocodile Input
SA9	-25.75917	27.80381	Dam
SA10	-25.70753	27.80922	Borehole
SA11	-25.68986	27.83967	Crocodile Output
SA12	-25.68986	27.83967	Tap
SA13	-25.77369	27.77106	Magalies Input
SA14	-25.72978	27.85472	Dam
SA15	-25.73333	27.86431	Dam
SA16	-25.73528	27.87197	Dam
SA17	-25.73928	27.88158	Dam
SA18	-25.75483	27.88769	Dam
SA19	-25.76303	27.89292	Dam
SA20	-25.76044	27.86878	Dam
SA21	-25.74844	27.86356	Dam
SA22	-25.74894	27.84817	Dam
SA23	-25.75433	27.82642	Dam
SA24	-25.76139	27.79783	Dam
SA25	-25.72592	27.79853	Dam
SA26	-25.74678	27.82403	Borehole
SA27	-25.74856	27.82228	Spring
SA28	-25.77922	27.84744	Borehole
SA29	-25.78192	27.85511	Borehole
SA30	-25.82533	27.81450	Borehole

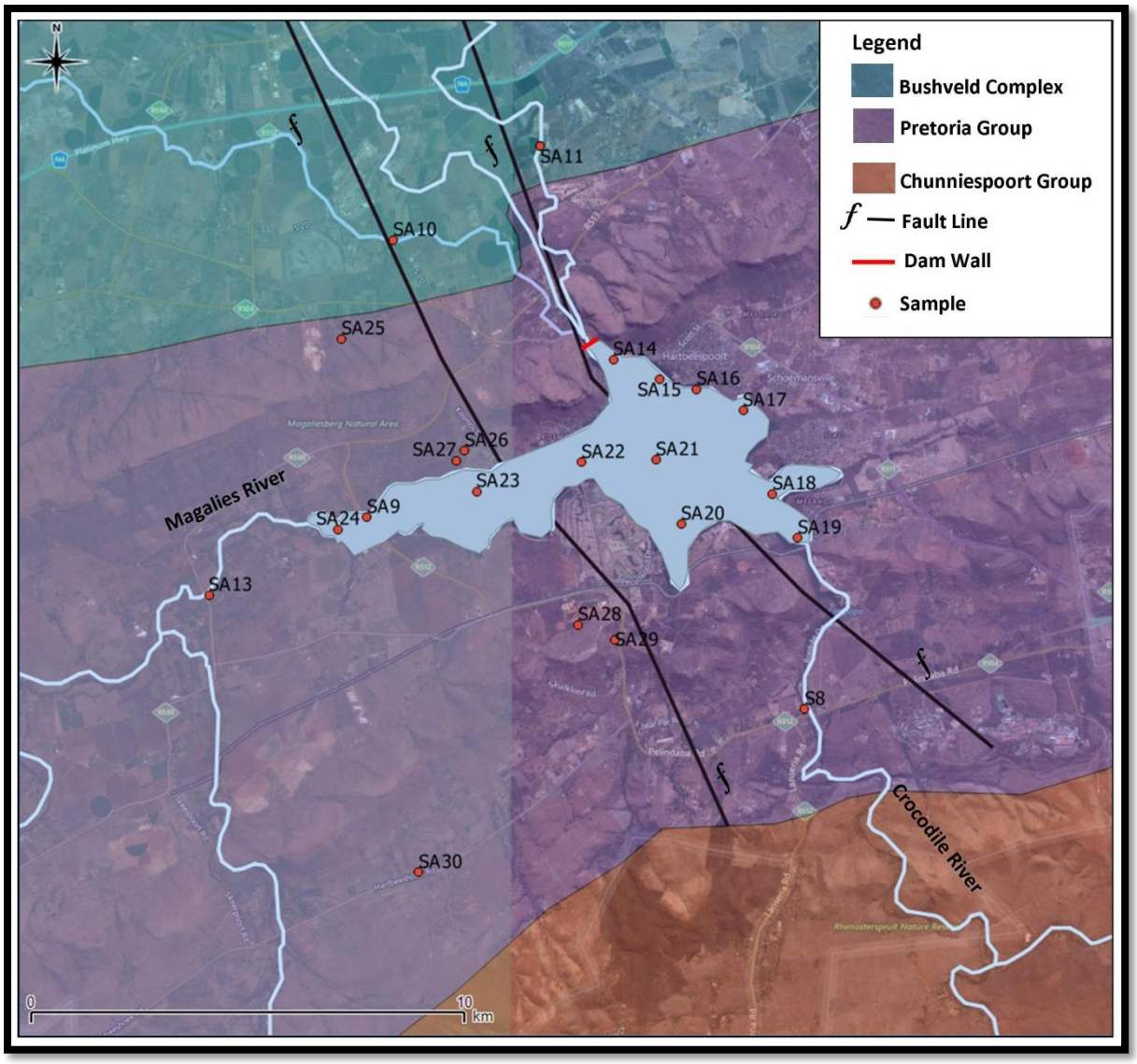

Figure 5: Sampling positions taken in June. Samples SA11 and SA12 are in the same position.

3.2 Sampling Preparation

Sampling bottles were deionized and prepared with sealable lids a day before. 1L bottles were used for tritium, 10ml bottles were used for $\delta^{18}O$ and $\delta^{2}H$ and 100ml bottles were used for metals. All field equipment was calibrated before field work. Gloves, a cooler box and black bags were used to ensure the integrity of the samples, to avoid fractionation by light and ensure personal safety from the samples. Satellite images, geological maps and a GPS were used to ensure planned samples could be located. A boat and a baler were pre-booked and two buckets and two lengths of nylon rope were taken with to ensure accessibility to samples.

3.3 Sampling Procedure

Aerial maps were used to assess preliminary sampling points which were noted and later recorded as GPS points in a field book. The conditions of the sample sites were also noted. Gloves were worn before samples were taken and sample bottles were rinsed 5 times with sample water and then filled to the brim; leaving no air bubbles before sealing. The bottles were labelled with sample name, date and type of sample and were cross referenced with the field note book. Samples were then put into light tight containers and loaded into the transport vehicle.

Field calibrated machines were used in order to reduce uncertainty with readings. These included the multi-parameter meter and the portable metal analyser, which were calibrated to standards. The measuring container was also rinsed with the sample 5 times in order to reduce contamination. Readings were done in the shade to avoid interference from solar radiation. All samples were taken using bottles rinsed in the sample water and thus no cross contamination occurred. The samples were put in black bags and cooler boxes to avoid fractionation and all samples were filled to the brim ensuring no air inside the sample. The stable isotopes were analysed using a Liquid Water Isotope Analyser using 6 standards to 3 standard deviations to ensure accuracy.

3.4 Physio-chemical Parameters

A multi-parameter meter was used to test physical parameters such as Electrical Conductivity, Total Dissolved Solids, temperature and pH balance of the samples. A dissolved oxygen meter was used to measure dissolved oxygen when the dry season samples were taken. These values were averaged and compared by sample type and season. Samples were also tested for physiochemical data in the field.

3.5 Environmental Isotopes

3.5.1 $\delta^{18}O$ and $\delta^{2}H$

Water samples for the measurement of $\delta^{18}O$ and $\delta^{2}H$ were collected with 10ml glass bottles with screw-top lids which were rinsed with sample water 5 times before filled leaving no air bubbles and clearly labelled. Samples were put in a cooler box and protected from light while transported to the laboratory.

The stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ were analysed by using the Liquid Water Isotope Analyzer-model 45-EP at the University of the Witwatersrand, South Africa. The instrument contains laser analysis system and an internal computer, Liquid auto-sampler, a small

membrane vacuum pump, and a room air intake line that passes air through a Drierite column for moisture removal. A Hamilton microliter syringe was used to inject 0.75 µL of sample through a PTFE septum in the auto-sampler. The injection port of the autosampler is heated to 46°C to help vaporize the sample under vacuum immediately upon injection. The vapour then travels down the transfer line into the pre-evacuated mirrored chamber for analysis. A 1 ml aliquot of a sample was pipetted into a 2 –mL auto-sampler glass vial and closed with PTFE septum caps. Five standards were used in the analysis procedure where the laser machine automatically calibrates itself and measures stable isotope values. The standards used and areas were as follows:

5C: δ^2H -9.2 ±0.5, $\delta^{18}O$ -2.69±0.15,

4C: δ^2H -51.6 ±0.5, $\delta^{18}O$ -7.94±0.15,

3C: δ^2H -97.3 ±0.5, $\delta^{18}O$ -13.39±0.15,

2C: δ^2H -123.7 ±0.5, $\delta^{18}O$ -16.24±0.15,

1C: δ^2H -154±0.5, $\delta^{18}O$ -19.49±0.15.

The laser machine is capable of providing accurate results with a precision of approximately 1 ‰ for δ^2H and 0.2 ‰ for $\delta^{18}O$ in liquid water samples of up to at least 1000 mg/L dissolved salt concentration. The machine uses Standard Mean Ocean Water (SMOW) and calculates values by inputting into the following formula(Harmon et al., 1985; IAEA, 1992):

$$\delta^{18}O = \left\{ \frac{\left(\frac{^{18}O}{^{16}O}\right)Sample}{\left(\frac{^{18}O}{^{16}O}\right)Standard} - 1 \right\} \times 1000 \text{ (‰)} \quad (6)$$

Similarly $^2H/^1H$ is used to calculate δ^2H in parts per thousand. These results were plotted against the Pretoria Local Meteoric Water Line or PLMWL represented by the following formula attained from GNIP (IAEA, 1992; IAEA/WMO, 2016)

:

$$\delta^2H = 7.05\delta^{18}O + 7.6 \text{ (‰)} \quad (7)$$

The samples were plotted by sample type and as a whole.

3.5.2 Tritium

For tritium sampling, bottles were rinsed with the sample water 5 times before filling a 1.5L bottle to the brim with the sample. These samples were clearly labelled and stored in black bags away from light.

Tritium samples were sent to the iThemba, Gauteng, for analysis on the 6th of June 2016. One was a spring sample, five were from boreholes, one was from a tap drawing borehole water, twelve were dam samples, two were river input samples and two were output samples. At iThemba Laboratory 500ml of the samples were distilled with sodium hydroxide and then enriched by electrolysis. An electric current was applied and the volume of water reduced to 20ml (Abiye et al., 2015). These samples were enriched by a factor of 20 and ready for liquid scintillation when half is mixed with 11ml of Ultima Gold and these are then counted by the machine (Abiye et al., 2015). The results were given in units of tritium units or TU.

These results were plotted with $\delta^{18}O$ to distinguish any overlapping data in the stable isotope system. These results were also plotted spatially with data from Abiye et al. (2015), Nkosi (2016) and data from samples retrieved from further upstream to show where the river gets contaminated.

The nuclear decay equation was applied to the calculations as a quality assessment. The manipulated decay equation applied is as follows:

$$t = h \times \frac{Log\left(\frac{A_{Sample}}{A_{Initial}}\right)}{Log\left(\frac{1}{2}\right)} \text{ in years} \quad (8)$$

Where

A_{Sample} is the amount of the sample left after time (t) has passed given in T.U.

$A_{initial}$ is the initial amount at the time of infiltration given in T.U.

t is the time taken from infiltration until a sample was taken or residence time in years

h is the specific half-life of the isotope in years given by Jenks et. al (1950)

The initial activity will be taken as the average value for rain tritium in Abiye et.al. (2015), which is stated to be 5.6 T.U.

3.6 Metals

Metals such as cadmium, copper and lead were analysed using a portable metal analyser called the PDV6000 Ultra. This machine uses Anodic Stripping Voltammetry or ASV - the heavy metal is collected on the surface of the one electrode and accumulates over time while an ionization potential is applied to the electrolyte. The other electrode is reduced. The current across the two electrodes is plotted as a voltammogram and produces a peak. This peak amplitude is measured and compared with known standards.

The metals were taken during both sampling seasons and were compared graphically using geographic information system (GIS).

3.7 Water Balance

The area chosen for investigation was Hartbeespoort Dam, which when modelled, looks like Figure 6.

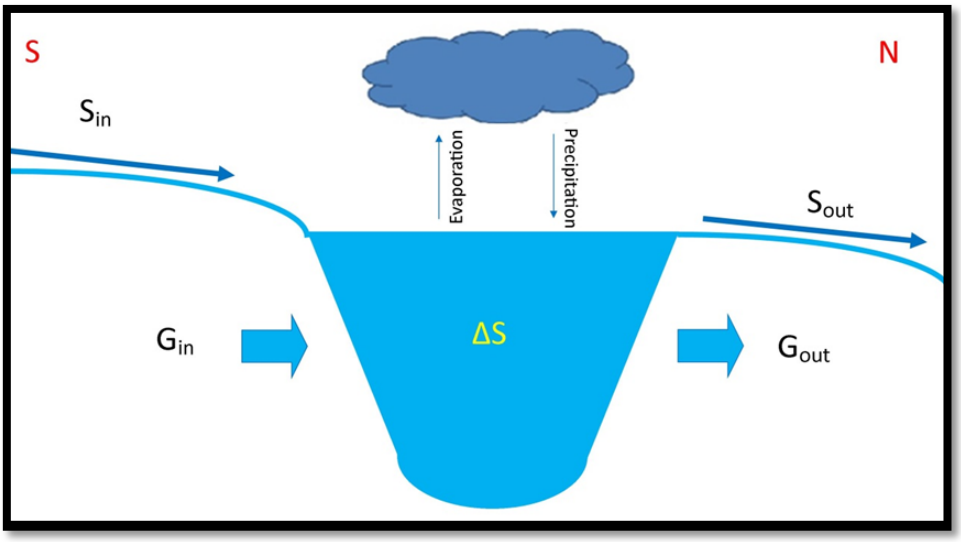

Figure 6: Water balance model to establish knowns and unknowns for the system.

Long term data was gathered for a 15 year period from the 1st of October 2001 until the 30th of September 2015. The purpose of this was to do a water balance.

This data was taken from the Department of Water and Sanitation database. The data collected was for surface water input, surface water output, precipitation, evaporation, water levels and percentage storage. The following stations were used:

Table 4: Table of monitoring stations used for the water balance

Crocodile River Surface Input	A2H012
Magalies River Surface Input	A2H013
Crocodile River Surface Output	A2H083
Precipitation	A2E012
Evaporation	A2E001

Evaporation data was recorded using a S-Pan. The water level and percentage storage data was used to calculate an average maximum water level. This was used as a multiplier for missing storage percentage data which was forward projected. The following formula was used for the water balance:

$$P + G_{in} + S_{in} - E - G_{out} - S_{out} - \text{Abs} \therefore \Delta G = \Delta S + E + S_{out} + Abstraction - P - S_{in} \ (m^{3)}) \qquad (10)$$

Where,

P is precipitation on the dam

E is evaporation on the dam

S_{in} is stream water flow in plus sewage

S_{out} is dam water flow out plus sewage

ΔG = G_{in}-G_{out}, are groundwater in and out

ΔS is the change in storage

Abstraction is the water extracted from the dam

All values were required in SI units of cubic meters to do this calculation. The evaporation and precipitation were given in millimetres and converted to meters. This required a surface area multiplier to convert it to cubic meters. The area at maximum dam capacity or 100% storage was taken to be 20km^2 as given in the SANSP 110 report (Ashton et al., 1985). This did not solve the surface area variability as dam capacity fluctuates. Thus the following formula was applied:

$$Actual\ Area = \frac{Area\ at\ Maximum\ Capacity \times \%\ Storage}{100}\ in\ m^2\ ) \qquad (11)$$

This ensured that the surface area variability with time was accounted for in the equation, assuming a one to one relationship existed between the maximum area and the % storage.

The actual area was multiplied with monthly values for evaporation and precipitation to calculate monthly volume values for evaporation and precipitation respectively. The equations used were:

$$Monthly\ Volume_{Evaporation} = Evaporation\ (m) \times Actual\ Area\ (m^2)\ ) \qquad (12)$$

And

$$Monthly\ Volume_{Precipitation} = Precipitation\ (m) \times Actual\ Area\ (m^2)\ ) \qquad (13)$$

The monthly volume for storage was calculated using the monthly changes in water level in meters, multiplied by the monthly area in square meters, to arrive at a monthly storage change.

Surface inputs and outputs were given as cubic meters.

Abstraction from the Crocodile River north of the Hartbeespoort Dam wall is seen in the table below.

Table 5: Sources of abstraction from the Crocodile River exiting the dam (WRC, 2012)**.**

PELINDA.ABS	0.84Mm^3
A2R001IND.ABS	0.00Mm^3
A2R001IRR.PRN	147.46Mm^3

This had a total of 148 300 000m^3 for 2012 (WRC, 2012) and an average of 105 600 000m^3 for the years of 1964-1978 (de Clerc, 2010). This was plotted on a scatter plot and an exponential equation was produced (equation 14). This was used to generate values within a -0.4% error or 0.4% underestimate.

$$Abstraction_{year} = 0.27e^{0.01 \times Year} \qquad (14)$$

These were averaged from 2000-2015 to produce a value for the long term water balance. For monthly variations, abstraction averages were divided by 12 for a particular year.

To attain yearly values of volume, the values for one hydrological cycle were summed together. This was done for a 15 year period, from October 2000 until September 2015. Each yearly parameter was compared on a scatter chart (Figure 20).

The values were then averaged for each parameter over the 15 year period. The two surface inputs; the Magalies and the Crocodile River input, were summed as a surface input. The yearly parameters were compared in order to observe which ones were the major contributors to the water balance. Monthly variability was assessed for detailed changes in groundwater change to assess seasonal variability. A water balance was done for every year to check errors in values and a percentage error was estimated.

3.8 Baseflow Separation

Once the difference in groundwater contribution has been estimated, the single parameter recursive digital filter method for baseflow separation with a fixed α of 0.95was applied in order to gather the average baseflow for the Magalies and Crocodile Rivers. These values were an average for a 15 year period from 01 October 2000 until the 30 September 2015. Once runoff is separated from the hydrograph, sewage will be subtracted in order to get true baseflow. This will be assumed to be the amount of water entering the dam and as the amount of baseflow which joins the Hartbeespoort dam as G_{inflow}

3.9 Groundwater contribution

Using the formula

$$\Delta G = G_{inflow} - G_{outflow}\ (m^3) \qquad (15)$$

And subsequently

$$G_{outflow} = G_{inflow} - \Delta G\ ) \qquad (16)$$

Where

$G_{outflow}$ is the water exiting the dam.

G_{inflow} is the water entering the dam as groundwater calculated by the baseflow separation method

ΔG is the change in groundwater calculated by the water balance.

Chapter 4 Results and discussion

4.1 Physical Parameters

The Electrical Conductivity, total dissolved solids and dissolved oxygen were mapped using GIS and showing areas with variable concentrations seen in figures 11, 12 and 13.

Comparatively higher EC value of 619 µS/cm, was derived from the upstream part of the Crocodile River than from the Magalies River, 450 µS/cm. This held true for the total dissolved solids, which has values of 307mg/L for the upstream Crocodile River with values of 208 mg/L for the Magalies River. There is also a relatively high value of total dissolved solids, 309 mg/L, just before the dam wall with a more dilute value, 258 mg/L, after the wall. On average the EC and TDS are higher in the month of June, than the month of March for all surface samples (see Table 4). The highest average TDS is found in the Crocodile River input and the lowest is found in the borehole samples.

The Crocodile River contributed the most EC and TDS, 619 µS/cm and 307mg/L, respectively, to the Hartbeespoort Dam. This could be from the accumulation of 715 400m^3 of sewage that enters the dam from this river each year. The Magalies River, which contributes hardly any sewage, has the least EC and TDS values of 450 µS/cm and 208 mg/L, respectively. The TDS from these rivers mix within the dam, collect at the dam wall and, when released through the sluice, dilute the original concentration of the Crocodile River to less concentrated dissolved solids. The dissolved solids could have accumulated at the dam wall and become heavy enough to sink and settle within the sediment. Wittman and Forstner (1975) support this with their sediment study of heavy metals. The sample collected during the rainy month of March also added more water in the form of precipitation and runoff, which can dilute true values. Since sampling in March was taken after heavy rain, samples taken during this time were not true representations of the EC and TDS compared to that of the dry winter month of June.

The dissolved oxygen was higher, 18.49mg/L in the Magalies River than in the upstream Crocodile River, which had a value of 17.6mg/L. The water leaving the dam had slightly lower values of 15.52mg/L and 17.6mg/L. High amounts, 18.08mg/L were observed from the spring but lower amounts of 14.39mg/L were observed from the groundwater 40m below the surface. Dissolved oxygen is highest in the Magalies River input and lowest in the Hartbeespoort Dam samples.

Dissolved oxygen (DO) is absorbed as gas in water, through movement and photosynthesis of aquatic flora, which is vital for the survival of aquatic life (Perlman, 2017). If DO is below crucial levels for life, desertification will occur as well as eutrophication (Perlman, 2017). Higher values in the rivers compared to the dam shows that it is moving to the stagnant Hartbeespoort Dam (Perlman, 2017). It could also be due to the presence of a concentration of sewage in the dam (Perlman, 2017). The lower values in the Crocodile River compared to that of the Magalies River is due to the presence of sewage in the Crocodile River. The lowest value was in the groundwater sample; this was due to stagnation and water fed from the dam.

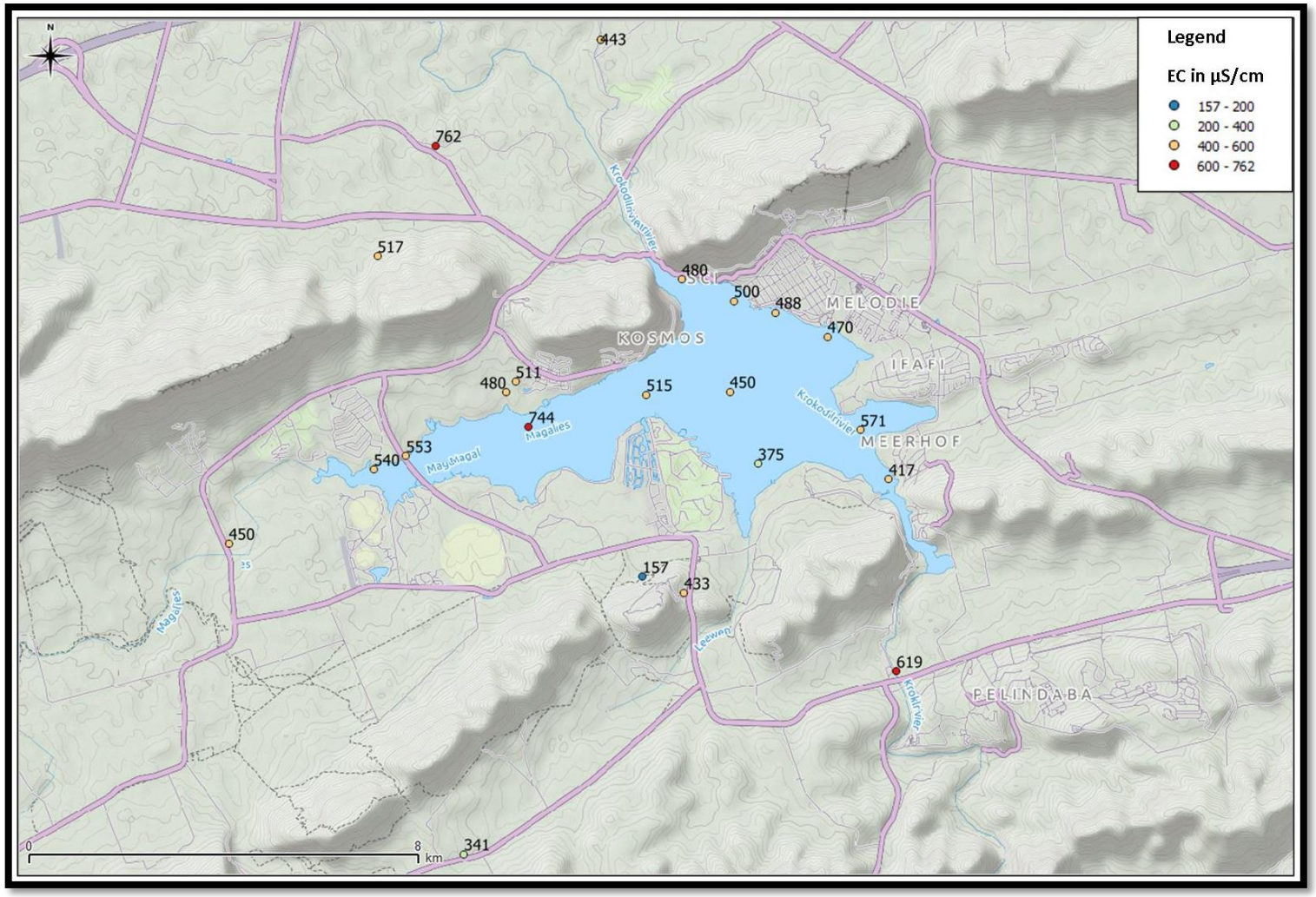

Figure 7: A GIS map of the Electrical Conductivity of the June samples taken in the Hartbeespoort Dam area.

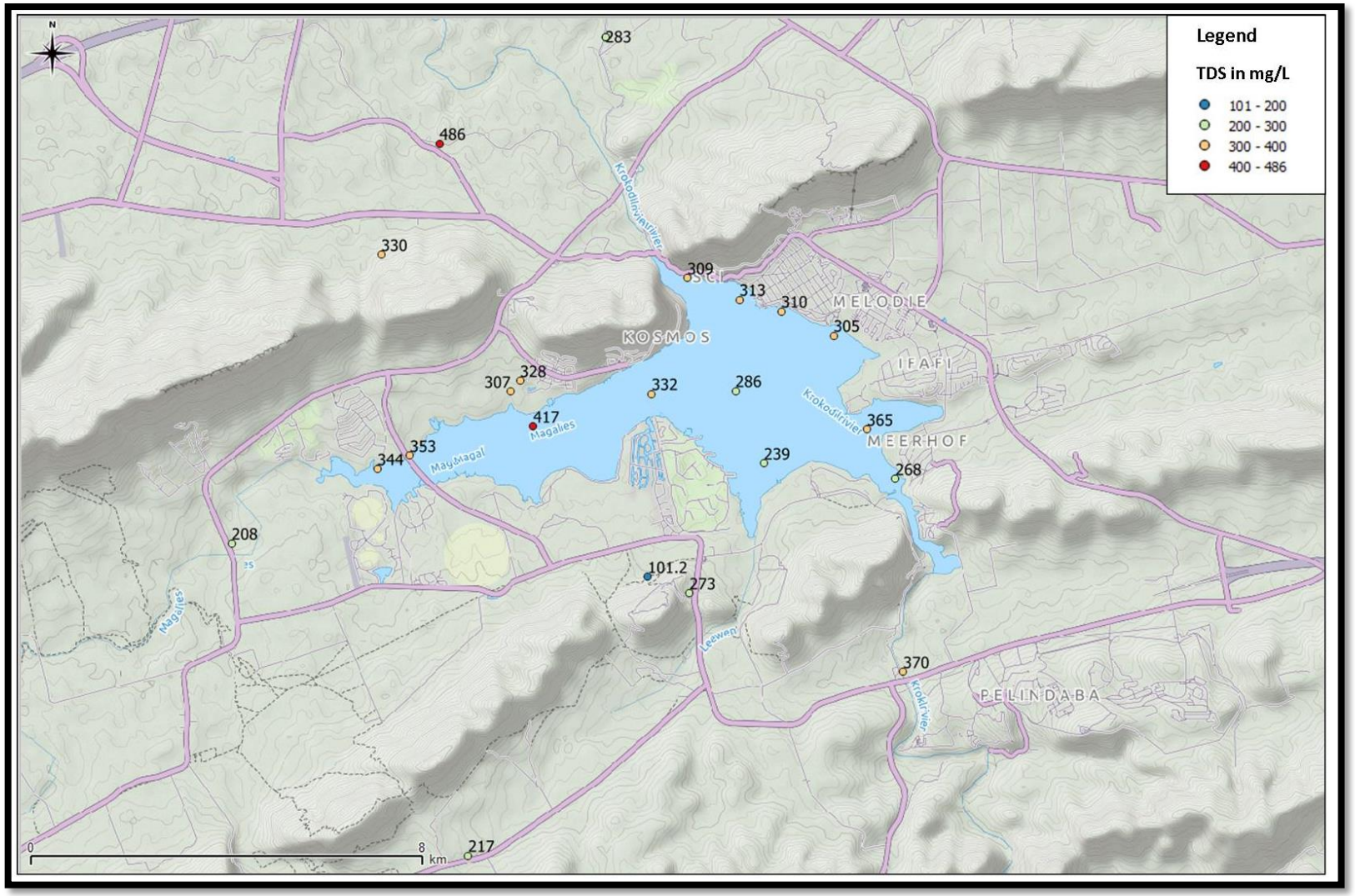

Figure 8: Total dissolved solids shown in a GIS map illustrating the spatial distribution.

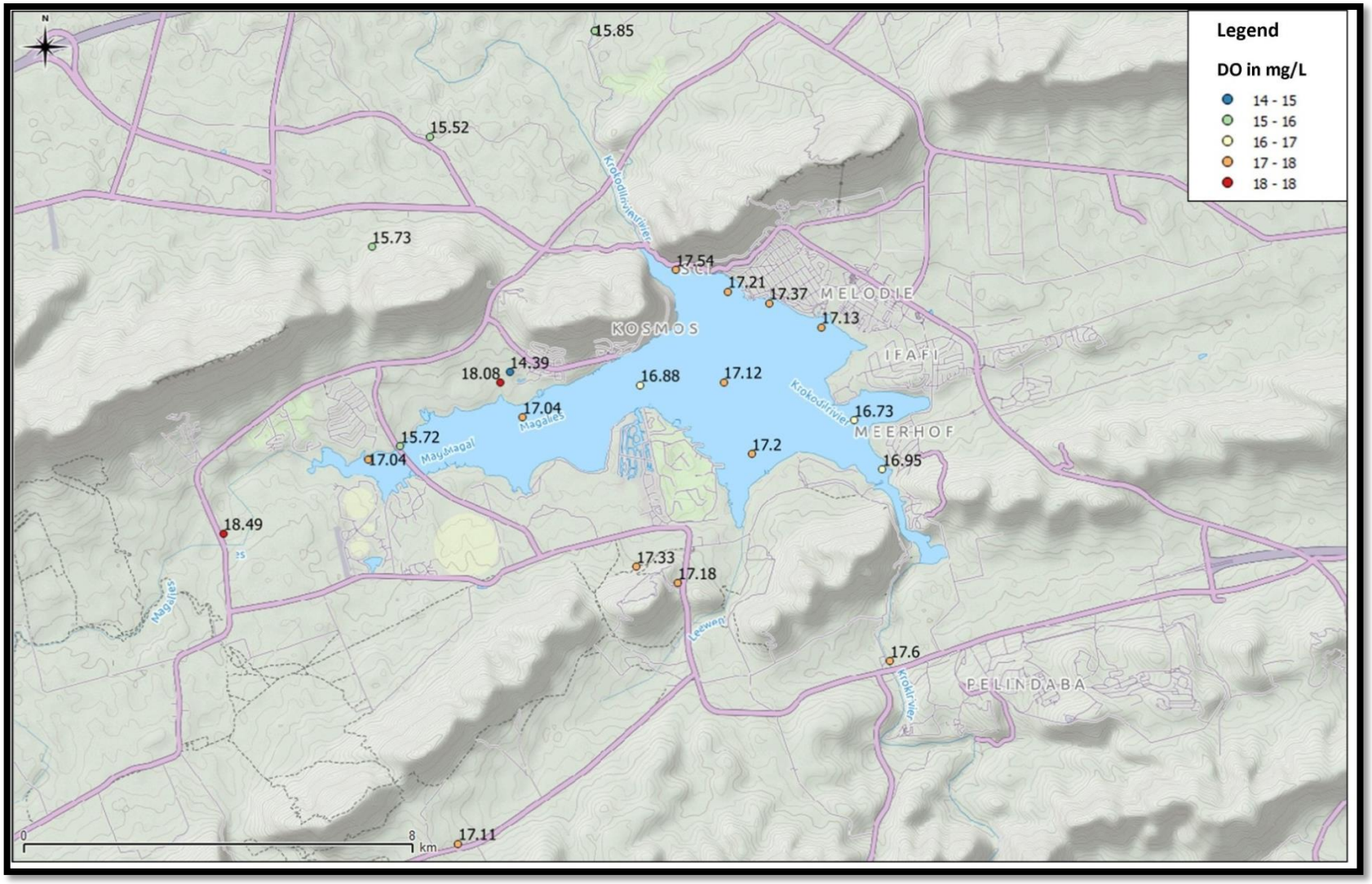

Figure 9: Dissolved oxygen GIS map showing the stagnation and presence of sewage.

Average values, as presented in table 6, show expected higher temperatures in the March summer rainy season than in the June dry winter season. In all samples the pH is more basic in the month of March than in the month of June.

The seasonal differences in pH of the water can be attributed to the additional water in summer as opposed to winter. As indicated in Table 6, the rivers are more basic in summer when there is less EC and TDS due to dilution from heavy rains. In winter there is less rain and thus the EC and TDS is higher while the pH of the water also becomes more acidic. This could also be due to the rivers being fed by mostly runoff water in summer and mainly groundwater in winter. It suggests that the groundwater may be more acidic than the surface water but the data suggests that the values are the same at a pH of 6.9. The borehole samples have the same trend in pH but slighter lower, 7.3 in summer, than that of the river, 7.7, and dam samples, 8.1. The EC and TDS have the opposite effect. This could indicate that the borehole samples are not mixing with the direct surface water and perhaps dispersed rather than focused recharge occurs in the area. The confirmation of whether or not mixing has taken place can be seen in the environmental isotope analysis in section 4.2.

Table 6: The average physical properties of samples.

	pH	EC(µS/cm)	TDS(mg/L)	T(^{0}C)	DO (mg/L)
March	7.8	361	231	27.1	-
March Crocodile River Input	7.7	397	254	25.2	-
March Crocodile River Output	8.3	210	136	28.0	-
March Dam Water	8.1	257	165	27.1	-
March Borehole Water	7.3	475	304	28.3	-
June	7.0	482	301	17.2	16.9
June Dam Water	6.9	509	321	17.2	16.9
June Borehole water	6.9	441	281	17.7	16.3
June Crocodile River Output	7.0	461	294	17.8	16.7
June Magalies River Input	6.8	450	208	15.6	18.5
June Crocodile River Input	6.9	619	370	15.2	17.6

4.2 Environmental Isotopes

Environmental isotopes were used to assess the physical processes in the Hartbeespoort Dam area.

The overall average values for stable isotopes indicate that in June the samples were more enriched with heavy isotopes (see Table 8). The dam samples show more enriched $\delta^{18}O$ in June than in March. The borehole water has more depleted $\delta^{18}O$ than that of the dam but less depleted than the Crocodile River for both the dry and wet seasons. The deuterium values are similar for both borehole and river samples. Tritium was therefore used to distinguish between the sources. The Crocodile River output indicates both $\delta^{18}O$ and $\delta^{2}H$ are highly enriched in June.

Table 7: Environmental isotopes taken in June.

Sample Name	δ 2H ‰	2H StDev	δ 18O ‰	18O StDev	Tritium (T.U.)	Tritium StDev
SA9	-6.14	0.00	-0.55	0.00	4.9	±0.4
SA10	-26.52	0.12	-4.79	0.04	1.3	±0.3
SA11	-1.99	0.25	3.19	0.09	5.7	±0.4
SA12	-2.11	0.00	3.00	0.00	5.5	±0.4
SA13	-31.46	0.00	-8.90	0.00	1.2	±0.3
SA14	-2.82	0.03	2.71	0.10	5.8	±0.4
SA15	-3.30	0.00	2.07	0.00	5.0	±0.4
SA16	-5.12	0.03	-0.32	0.00	5.6	±0.4
SA17	-2.90	0.16	2.88	0.05	6.0	±0.4
SA18	-2.74	0.12	2.58	0.07	6.0	±0.4
SA19	-4.49	0.00	-0.45	0.00	6.1	±0.4
SA20	-4.93	0.00	-0.37	0.00	5.6	±0.4
SA21	-5.14	0.06	-0.50	0.12	6.6	±0.4
SA22	-4.90	0.14	-0.66	0.04	6.2	±0.5
SA23	-5.68	0.08	-0.69	0.02	5.4	±0.4
SA24	-6.02	0.00	-0.40	0.00	6.5	±0.5
SA25	-4.84	0.00	-0.58	0.00	5.2	±0.4
SA26	-6.88	0.34	1.58	0.03	4.8	±0.4
SA27	-2.13	0.25	3.60	0.11	5.6	±0.4
SA28	-39.34	0.40	-12.65	0.10	3.3	±0.4
SA29	-38.18	0.12	-13.47	0.03	1.3	±0.3
SA30	-32.76	0.07	-9.76	0.04	1.9	±0.3

Table 8: The average stable isotope values for the samples taken in both March and June.

	δ 2H‰	± 2H StDev	δ 18O‰	± 18O StDev
March	-20.6	0.10	-4.6	0.05

March Crocodile River Input	-37.4	0.07	-6.6	0.07
March Crocodile River Output	-35.2	0.12	-6.3	0.07
March Dam Water	-4.7	0.00	-2.6	0.00
March Borehole Water	-31.2	0.18	-6.4	0.11
June	-10.9	0.10	-1.5	0.04
June Dam Water	-4.5	0.05	0.4	0.03
June Borehole water	-28.7	0.21	-7.8	0.05
June Crocodile River Output	-3.4	0.13	1.3	0.05
June Magalies River Input	-31.5	0.00	-8.9	0.00

The average values of the surface water show that the more enriched isotopes occurred during the June sampling period which has on average less precipitation. The borehole water in March has similar average isotopes to the surface water showing a similar source (rainfall). In June it is only similar to the Magalies River water but in the Crocodile River surface water has different sources. The dam water is always enriched with heavy isotopes compared to the streams and groundwater as a result of evaporation. This indicates evaporation is the prime physical process in the dam and leaving behind the heavier isotopes in the dam water.

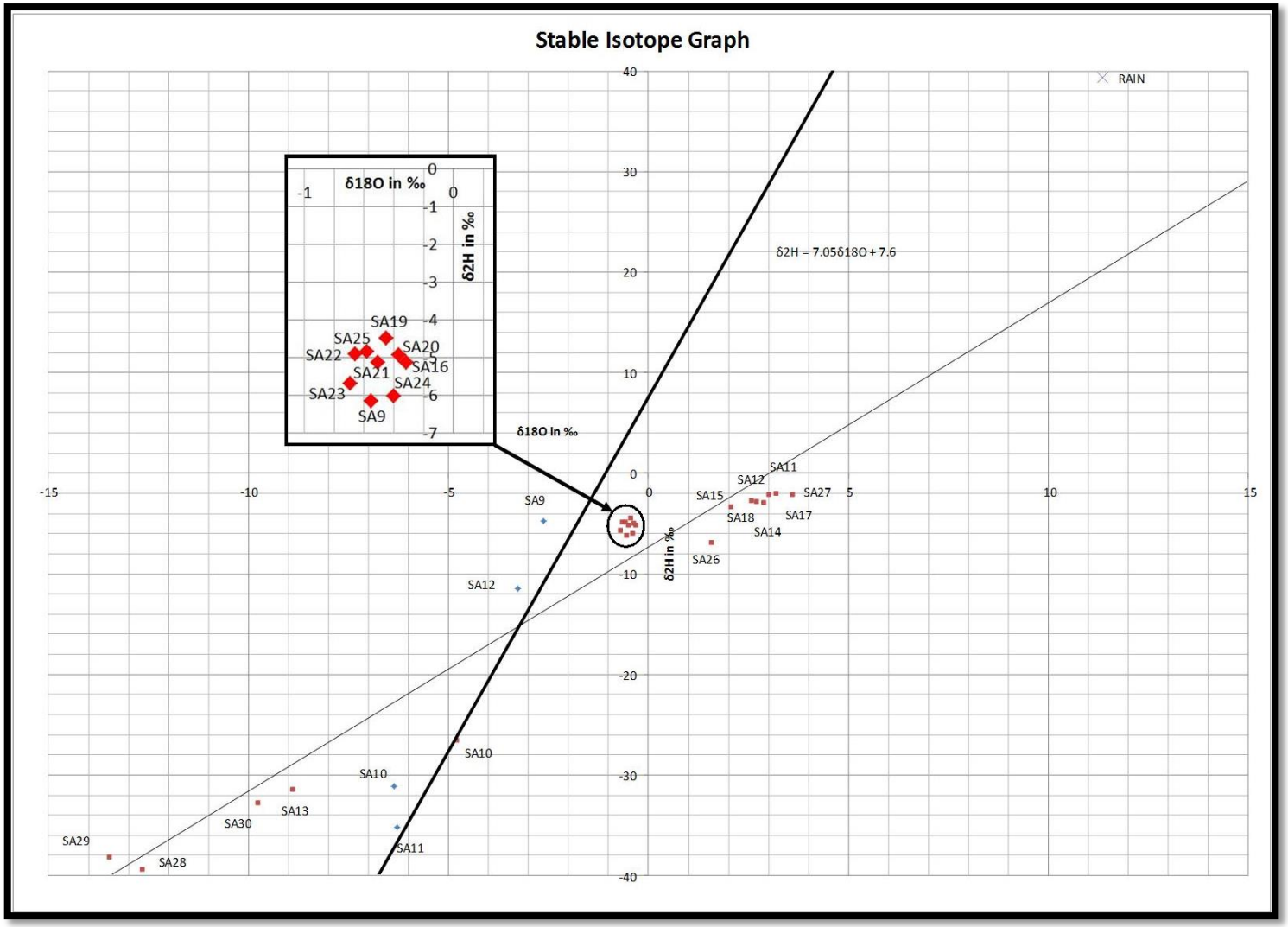

Figure 10: Stable isotope data plotted in relation to PLMWL.

The Pretoria Local Meteoric Water Line (PLMWL) (IAEA-GNIP, 2016), in Figure 14, was used to compare the systems as well as a rain samples from the study area. The samples in blue are representative of the March samples. These follow the PLMWL and show visible influence of rain, which fall above the LMWL. The June samples digress from the PLMWL indicating an evaporation effect from all samples except SA13, SA28, SA29 and SA30. The Johannesburg rain sample falls on neither line but is closer to the Hartbeespoort water line.

The summer samples in the month of March are related to the amount of rainfall. As expected, after a down-pour it is either rain water that was sampled or the groundwater which is feeding the surface water in summer, or the mixture of both. The groundwater sample falls on the local meteoric water line but since only one sample was taken. It is difficult to conclude that the contribution of groundwater to the surface water in March due to the dominance of surface runoff. The surface water in March falls on the Pretorian Meteoric Water Line and thus suggests recent rainfall as reflected in the figure 14. An observation of the difference in seasonality, dry and wet season, and a comparison to the PMWL indicates a regression in the month of June. This shows both the groundwater and surface water are being fed from a source other than that of the rainfall in Pretoria.

The Hartbeespoort Dam samples, as seen in Figure 14, show a digression from the PLMWL to the right in dry winter months indicating the effects of evaporation.

The upstream Crocodile River samples taken in June show the above-mentioned digression which indicates a feeding-source other than the Pretoria precipitation. The digression from the local meteoric water line in the Crocodile River compared to the Magalies River samples show very different isotopic signature. This is due to the input of sewage which mixes with the Crocodile River to a greater degree than that of the Magalies River

The borehole samples taken in June show a digression from the local meteoric water line and a different source than that of the local rain water. The spring sample plots along the same water line as the borehole samples which suggests a source similar to that of the boreholes but the tritium, as seen in figure 15, suggests rain water as a source. Mixing is taking place near the spring which occurs on the Brits Graben normal fault zone.

The environmental isotopic information for June is given in Table 7. Tritium was plotted against $\delta^{18}O$, in Figure 15, to distinguish sources as well as mixing processes. These were further plotted against Nkosi's (2016) borehole samples and slimes dam sample to see if there

were any connections. The use of Abiye et. al.'s (2015) dam data, average dolomite spring data, average borehole data, average stream data and average acid mine water data was used to establish further connections.

Sample 26 is plotted along the PMWL for both seasons, thus the tritium results would need to confirm the source. Sample 26 plots with the dam water samples and not the deeper borehole samples in the area on the tritium graph in Figure 15. This indicates that the borehole at sample 26 is being fed by the dam. The spatial position of sample 26, in Figure 9, further supports this.

The tritium isotope graph shows that the winter surface samples, except in the Magalies River, and all the borehole samples, except sample 26, are from two separate sources. The majority of the borehole samples are separated from the dam water. The Hartbeespoort Dam water shows elevated amounts of tritium, above local rainfall amount of 5TU, but when comparing it to the values from Abiye et al. (2015), it is much lower. This is because the source of tritium is not consistent. An average value of 12.73 T.U. ±0.7 for Hartbeespoort Dam tritium was found by Abiye et al. (2015), while the dam samples in June had an average of 5.8 T.U±0.42 which is less than half. This indicates that the tritium source in the area is strictly following waste water discharge regulation.

The differences between the Magalies River and Crocodile River sources are further demonstrated in Figure 15 where the Magalies River has the same source as the boreholes while the Crocodile River is feeding the dam.

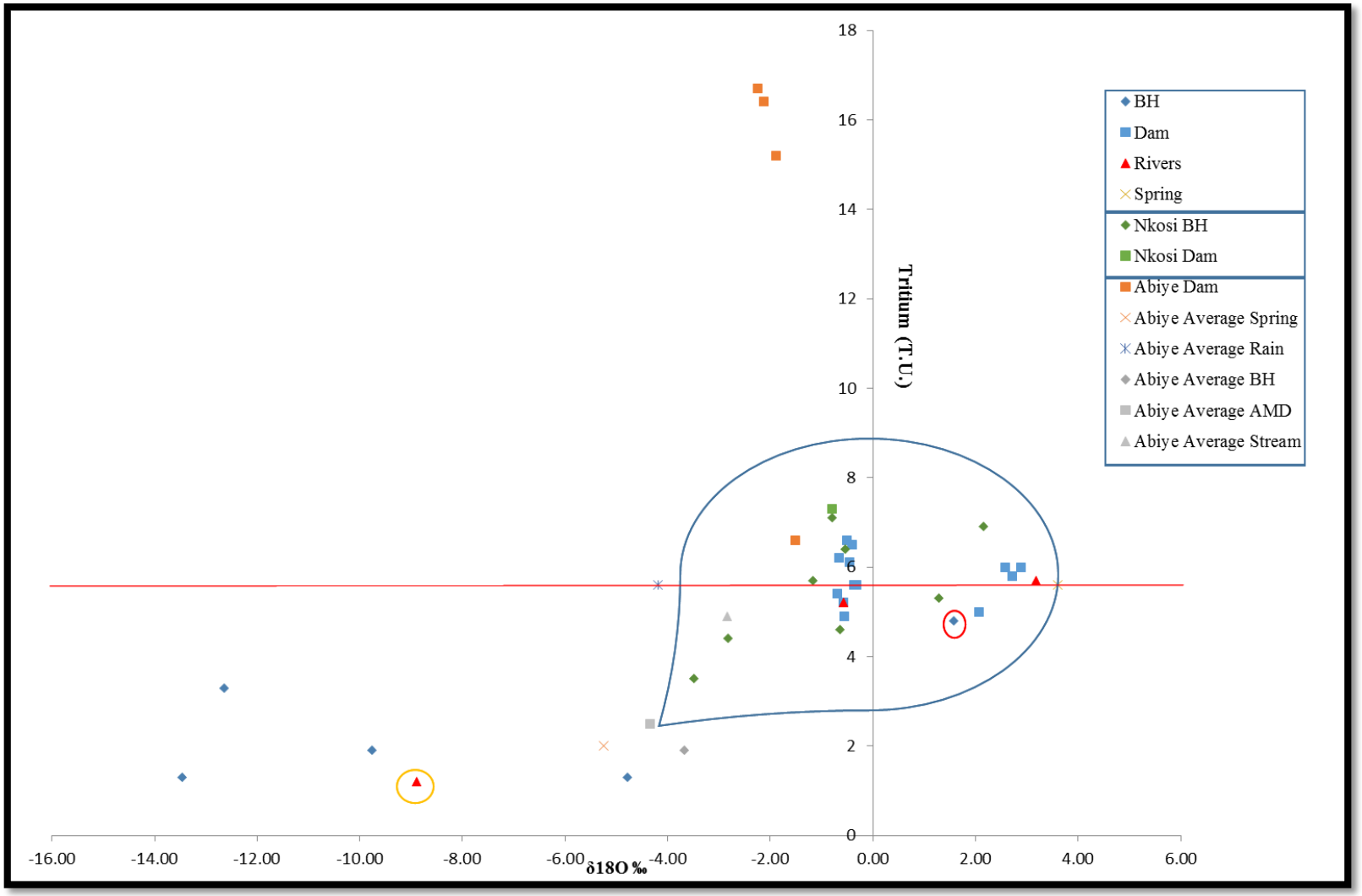

Figure 11: Tritium data plotted against $\delta^{18}O$ from the samples taken in June as well as, Nkosi (2016) and Abiye et.al. (2015)

When comparing the results to the Nkosi's (2016) and Abiye et al.'s (2015) data mixing of surface and groundwater is clearly occurring further north. The source of mixing, indicated by Nkosi's (2016) data, is artificial as the dam water is used for agricultural purposes. The tritium map information in section 4.3 details this.

4.3 Tritium

Tritium was mapped to show the spatial variation coming in and out of the dam as seen in Figure16. Using GIS platform, the tritium values are higher than 5.6 T.U., or average precipitation values in the region according to Abiye et.al. (2015), was mapped for the distribution using spatial vectors to understand the contamination paths in Figure 16. The surface values were checked for contamination using a radioactive decay method. The values were compared spatially with Nkosi's (2016) and Abiye et al.'s (2015) data.

The map shows that 54% of the samples taken in the dam were above 5.6 T.U. and 85% were above 5.0 T.U. indicating that contamination had taken place. The average tritium concentration for the dam was 5.8 T.U±0.42, which is above atmospheric levels. It therefore indicates contamination by anthropogenic inputs.

. Radionuclides are only reduced by nuclear decay or a change in the input function. The amount of decay needed, for a constant input function of a sample of 12.73 T.U. ±0.7 to reach 5.8 T.U±0.42 is approximately 14 years which is not consistent with the data. Thus the only other explanation is that the input function is inconsistent over time.

The map shows that the groundwater samples, except for sample 26, may be unaffected by contamination or have been in circulation longer than the surface samples. The Crocodile River sample is more elevated than the average stream values gathered by Abiye et al. (2015). This is where mixing of contaminated and uncontaminated water is taking place. The anthropogenic source is Pelindaba Nuclear Power Plant, as suggested by Abiye et al. (2015), which is spatially well positioned to contaminate the river system. The contamination could enter via the fault or through runoff into the Crocodile River but it is most likely a combination of both. Further downstream of the Hartbeespoort Dam, water has returned to the river via agricultural return flow from the dam water as Abiye et al. (2015) suggested.

The contamination further downstream, where Nkosi's (2016) data was sampled from, indicated the same isotopic signatures as the dam water and mixing with ground water. This process occurs by return flow from irrigation waters collected from the dam and mixing with

the baseflow. Nkosi (2016) attributed the contamination of the samples to the agricultural return flow and mining and speculated the source to be Hartbeespoort Dam. This was confirmed from the environmental isotopes.

. It is more likely that over pumping from mining areas have increased the cone of depression and have lowered the water table and drawn the waters traveling along the Brits Graben faults into the groundwater of Nkosi's (2016) boreholes like a fault water capture. This in combination with agricultural return flow would explain his data (Nkosi, 2016).

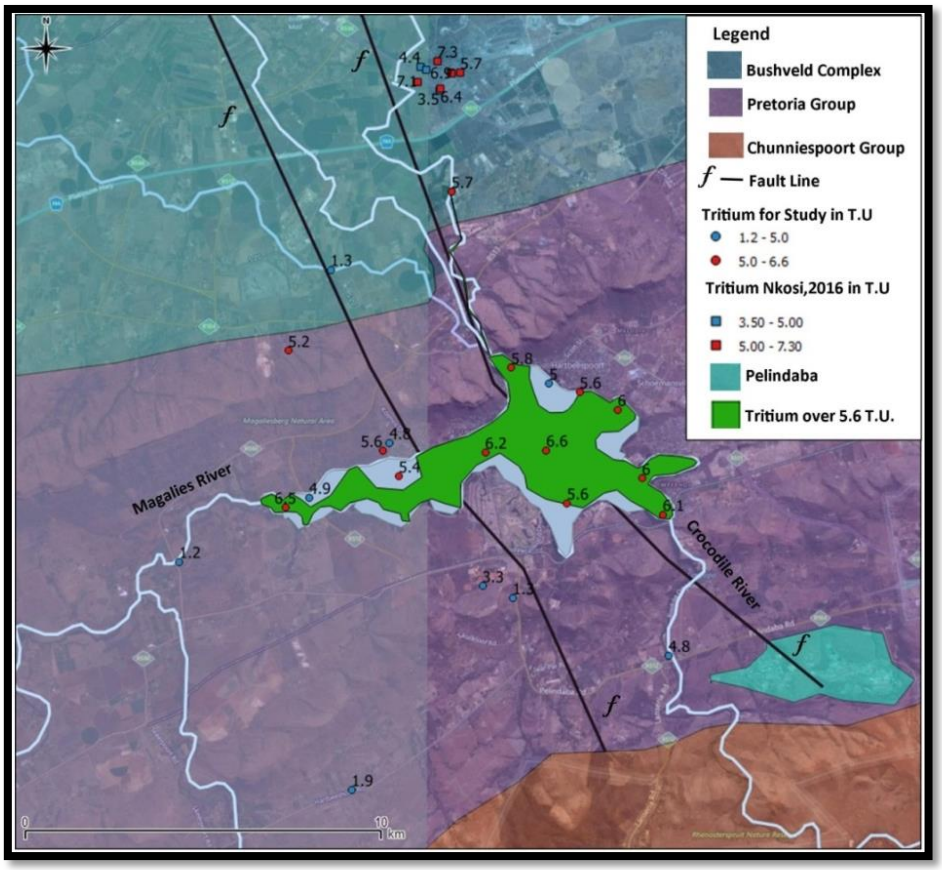

Figure 12: Map to show contamination of tritium above that of the average atmospheric tritium experienced in Johannesburg.

4.4 Metals

Limited samples were tested for cadmium, lead and copper. Almost all samples taken in March gave a result of zero which might be due to dilution by rain water (sampling was conducted right after rainfall).

Samples tested for heavy metals were averaged (Table 9). The Hartbeespoort Dam samples concentrated all metal values, however copper was higher in the borehole samples. The Magalies River has more lead than cadmium and copper.

Table 9: Average metal values

	Cadmium (ppb)	Lead (ppb)	Copper (ppb)
March Crocodile River Input	0	22.11	0
March Crocodile River Output	0	0	0
March Dam Water	0	0	0
June Dam Water	2.6	4.4	4.3
June Borehole water	2.1	2.6	5.8
June Crocodile River Output	2.5	1.8	3.1
June Magalies River Input	2.2	3.8	0.0

The Hartbeespoort Dam samples had the most metals on average except for copper, which was greatest in borehole samples. The concentration of metals in the dam has been attributed to thereaction and settling of particles in the sediment. The spatial relationships of the samples, in Figure 17 and 19 show a distinct pattern of Cd and Cu metal concentration from the inflow of the Crocodile River south of the dam to the dam wall. This is also shown to be present in the sediment samples from Wittman and Forstner (1975). The concentration of Pb, in Figure 18, is at the greater depths of the Hartbeespoort Dam.

The higher copper values in the borehole samples has been related to the water –rock interaction process in the area. The high lead value in the Magalies River samples indicate that there is some input of diesel into the river further upstream but this value is much less than the value coming from the Crocodile River in March. There is also settling of lead particles in the deeper parts of the dam.

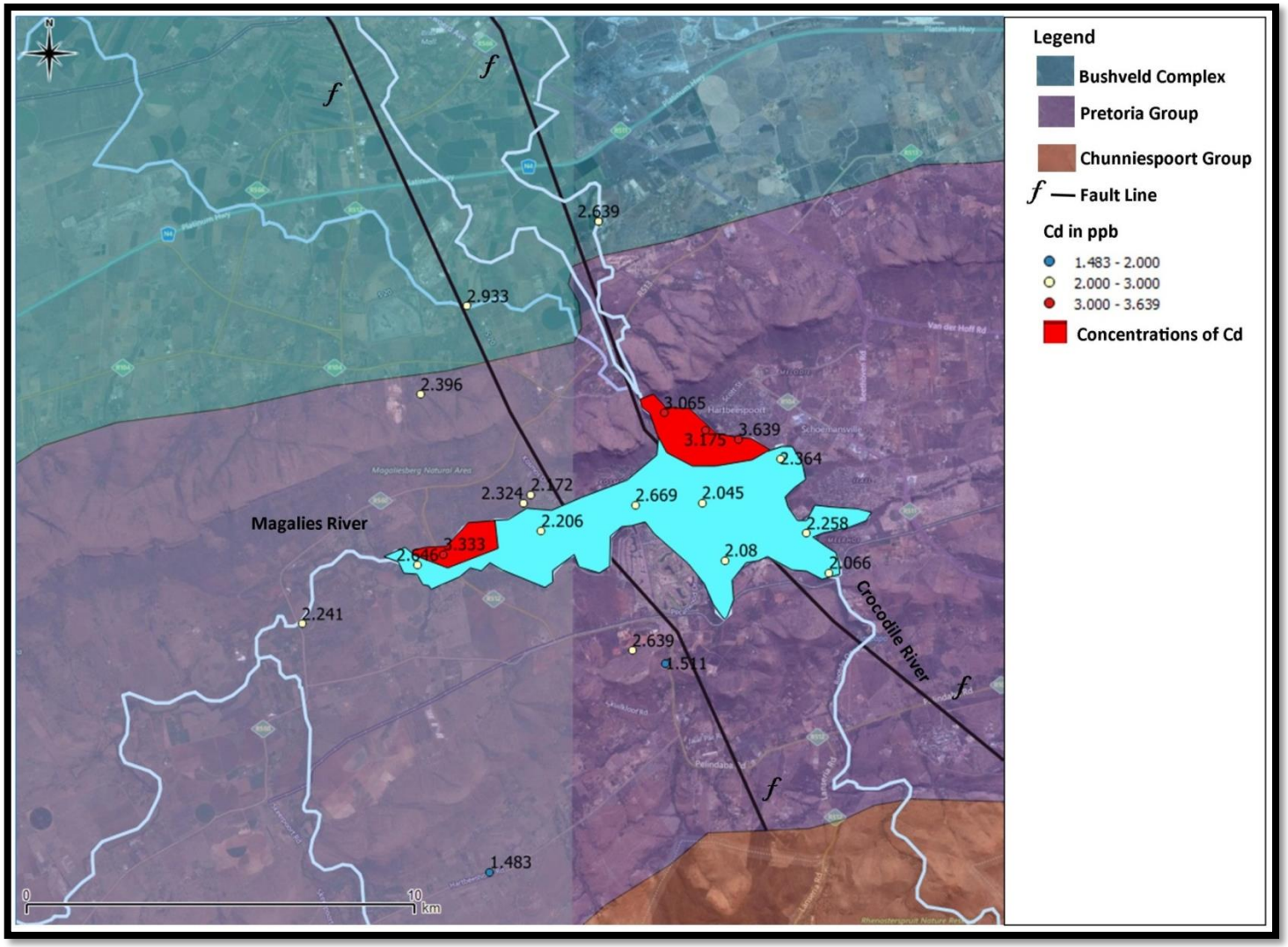

Figure 13: Cd in ppb distributed in the sample area.

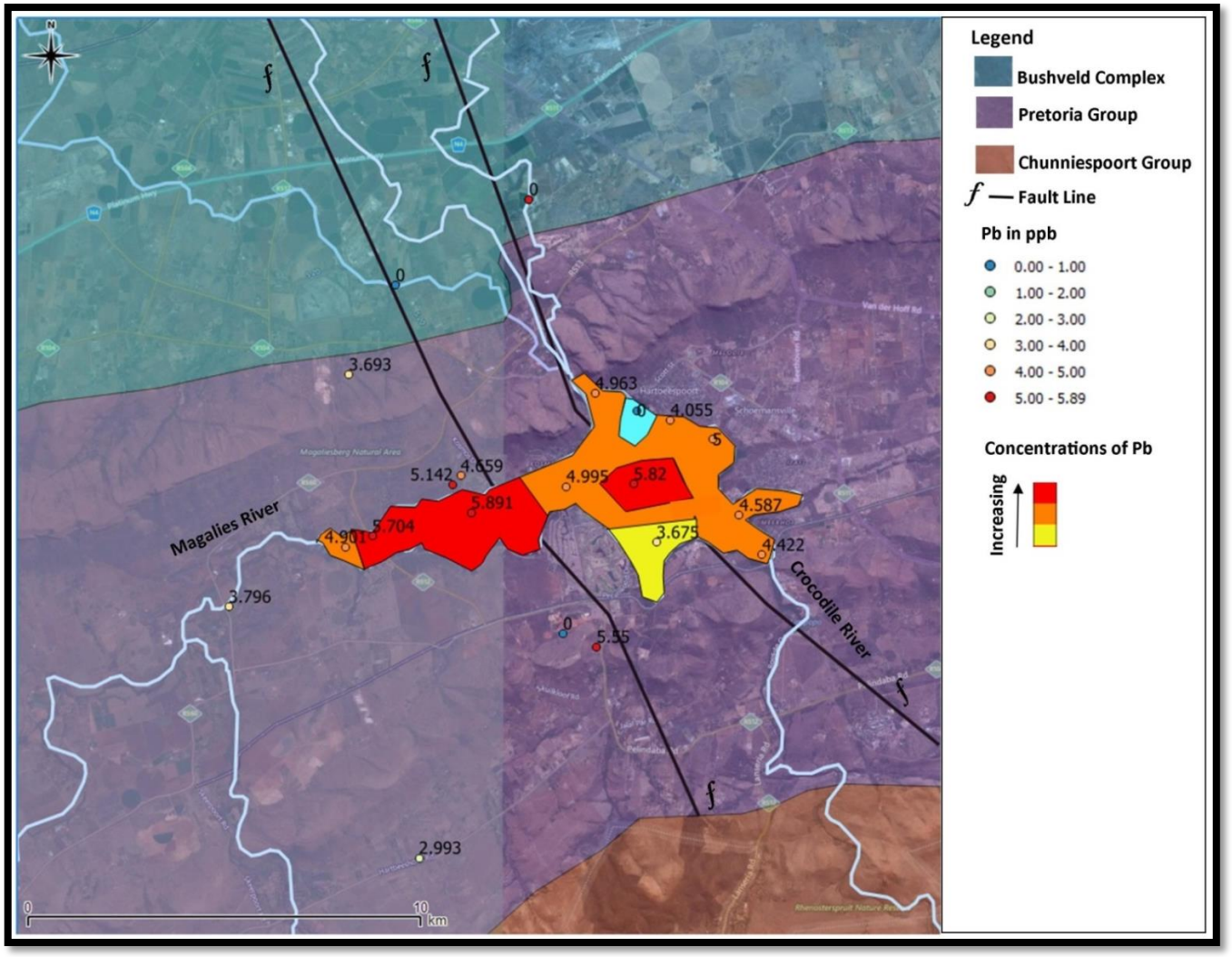

Figure 14: The spatial distribution of Pb in ppb which shows a concentration at the dam wall.

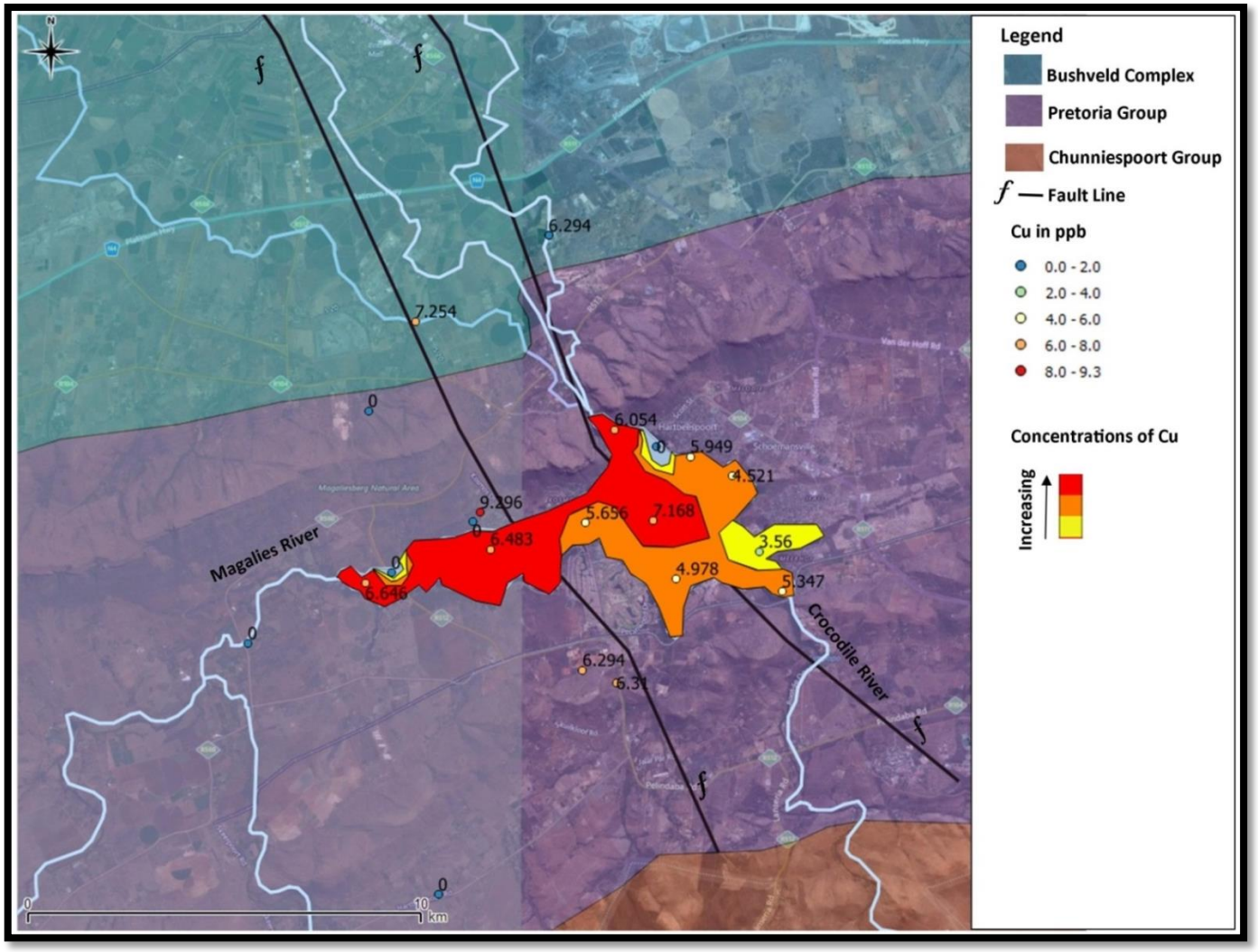

Figure 15: Map of the concentration of Cu in ppb within the June samples.

4.5 Dam Water Balance

Spatial and temporal boundaries were set using the most complete and available monitoring stations and the most recent long term time period as seen in Table 4. A model, Figure 10, was created in order to visualize the problem and numerically represent it in the formula, Equation 10, for a basic water balance method. This was applied to gather information on the change in groundwater of Hartbeespoort Dam. Quality controlled numerical averages were used to generate missing data.

The water balance was calculated over a 15 year period. The average change in groundwater is displayed in Table 10. This indicated an average gain of 18 million m^3 of water per year which was greater than the groundwater that exited the dam.

Table 10: Average yearly water balance to calculate the average change in groundwater 2000 to 2015.

ΔS m^3	E m^3	S_{out} m^3	P m^3	S_{in} m^3	Abstraction m^3	ΔG m^3
-394 801	30 435 186	293 124 000	12 848 855	433 317 133	141 347 076	18 345 472

The average ΔG calculated by the water balance over the past 15 years is 18 345 472m^3, with an error of 3.9% , which includes sewage. The sewage entering the system is assumed to be the same amount as that exiting. Sources of water gain could be from the addition of sewage which is unaccounted for in the water balance equation.

The annual variation was calculated and the variation of each parameter was compared in Figure 20. The major contributors of each year were the upstream Crocodile River followed closely by the Crocodile River downstream of the dam which is a human controlled system. The Crocodile River contributed the most water to the dam over the past 15 years yet there was no significant change in precipitation. This indicates that effluents must be adding to the river in order to create such a significant figure above that of the Magalies River. The change in groundwater is variable but since 2005 it has fluctuated between 50Mm^3 of a greater loss or gain of groundwater. The storage remains relatively constant throughout the year. The relative stability of the change in storage is due to the amount of effluents entering the dam through the Crocodile River as well as the return flow from agricultural runoff and the control of the sluice.

The monthly variability, in Figure 21, showed a general trend of progressive reduction of ΔG for the past 15 years. Monthly variability by hydrological year, over the 15 year period, showed that the amount of groundwater entering the dam is decreasing compared to the amount exiting the dam. The ΔG has decreased by approximately a 10 million m^3 drop in volume over the past 15 years.

The sources of water loss could be natural and anthropogenic. The natural sources would not have changed over time unless aided by anthropogenic means considering tectonic stability in the area. Pumping from boreholes for agricultural, private or mining, leads to cones of depression which lower the groundwater table, during dry months, and increases distance from the dam to the water table. This increases the amount of water which leaves the dam through the ground. The lowering of the water table downstream could also cause the water flowing along faults to be drawn from the dam at a faster rate, thus increasing the amount of water leaving the dam through the ground. This, together with the natural lowering of the groundwater by the normal faults of the Brits Graben creates a gravity driven flow.

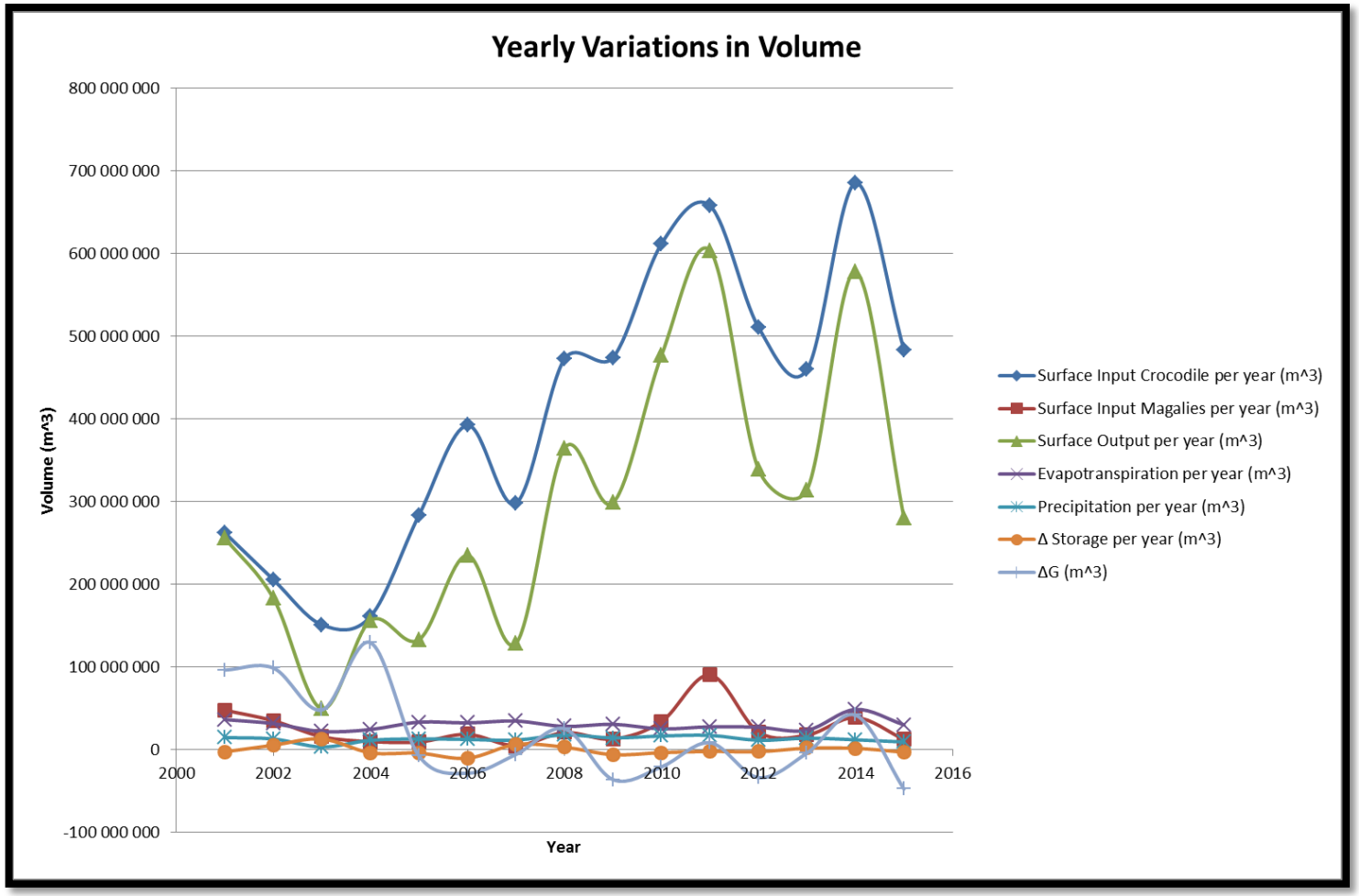

Figure 16: The yearly variation of each parameter of the water balance illustrating that the Crocodile River adds the most water due to effluents. The change in groundwater is variable but since 2005 has been between 50Mm^3 and -50Mm^3.

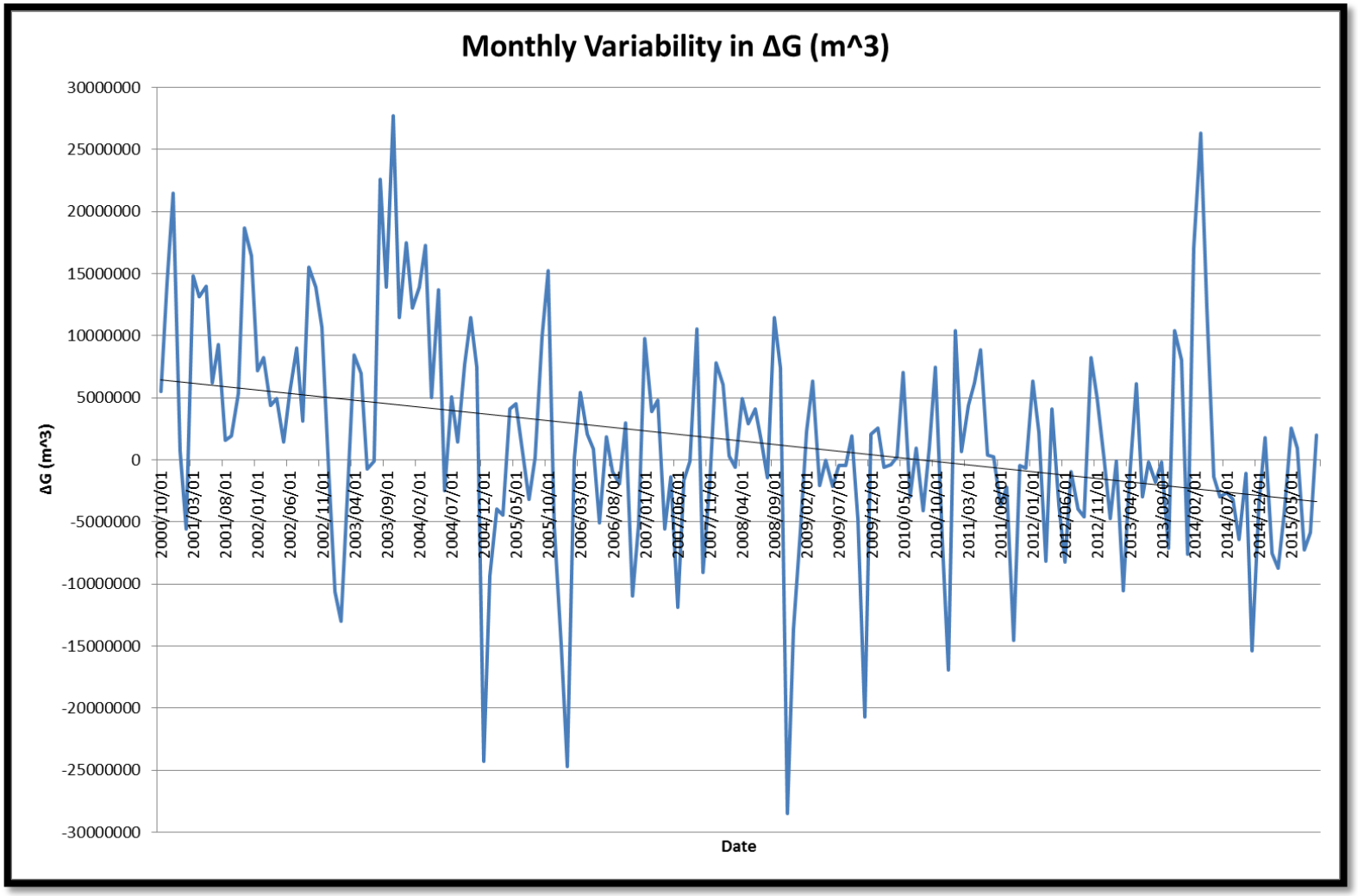

Figure 17: The monthly variability of the change in groundwater shows an increasing amount of water entering the dam but at a gradual rate.

Seasonal variations show that during most years the difference in groundwater is greater in the dry months than in the wet months. Mining extracts a constant amount of water but agriculture adjusts for water shortages by pumping groundwater or using private reservoir water collected in the wet season. The greater loss of groundwater from the dam in the dry season can be from agricultural abstraction.

The steady increase between the groundwater output and groundwater input over the 15 year period could be due to the growing population and concomitant demand on agricultural expansion which leads to over-pumping practices during dry months or years.

4.6 Baseflow Separation

The Crocodile River inflow, taken at measuring station A2H012 and shown in Figure 22, from 01 October 2000 to the 30 September 2015 using daily data in a single parameter recursive digital filter for baseflow separation. The missing data in 2004 and 2006 does not influence the long term results. The baseflow in the Crocodile River was inflated by sewage and needs to be subtracted from the baseflow separation as seen in Table 11.

Table 11: The average baseflow for the Crocodile River flowing into Hartbeespoort Dam

Year	Average Baseflow (m^3/s)	Baseflow (m^3)	Sewage (Ml/day)	Sewage (m^3/sec)	Sewage (m^3)	Gw In (m^3)
2000-2015	8.75	275 782 320	707.00	8.18	258 055 000	17 727 320

The Magalies River inflow was calculated using the daily discharge of A2H013, displayed in Figure 23, from 01 October 2000 to the 30 September 2015. There was no missing data. The Magalies River, in Table 12, showed an average value for baseflow, over the past 15years.

Table 12: Average value for baseflow flowing into the Hartbeespoort Dam.

Year	Baseflow(m3/s)	Baseflow (m3)	Sewage (m3)	Gw In (m3)
2000-2015	0.469	14 790 384.00	0	14 790 384

There are two more streams, the Leeuspruit and the Swartspruit, which contribute to the baseflow and hence the $G_{inflow.}$ This is not considered in these calculations due to its small contribution of water to Hartbeespoort dam. It should be noted that this would reduce the G_{out}.

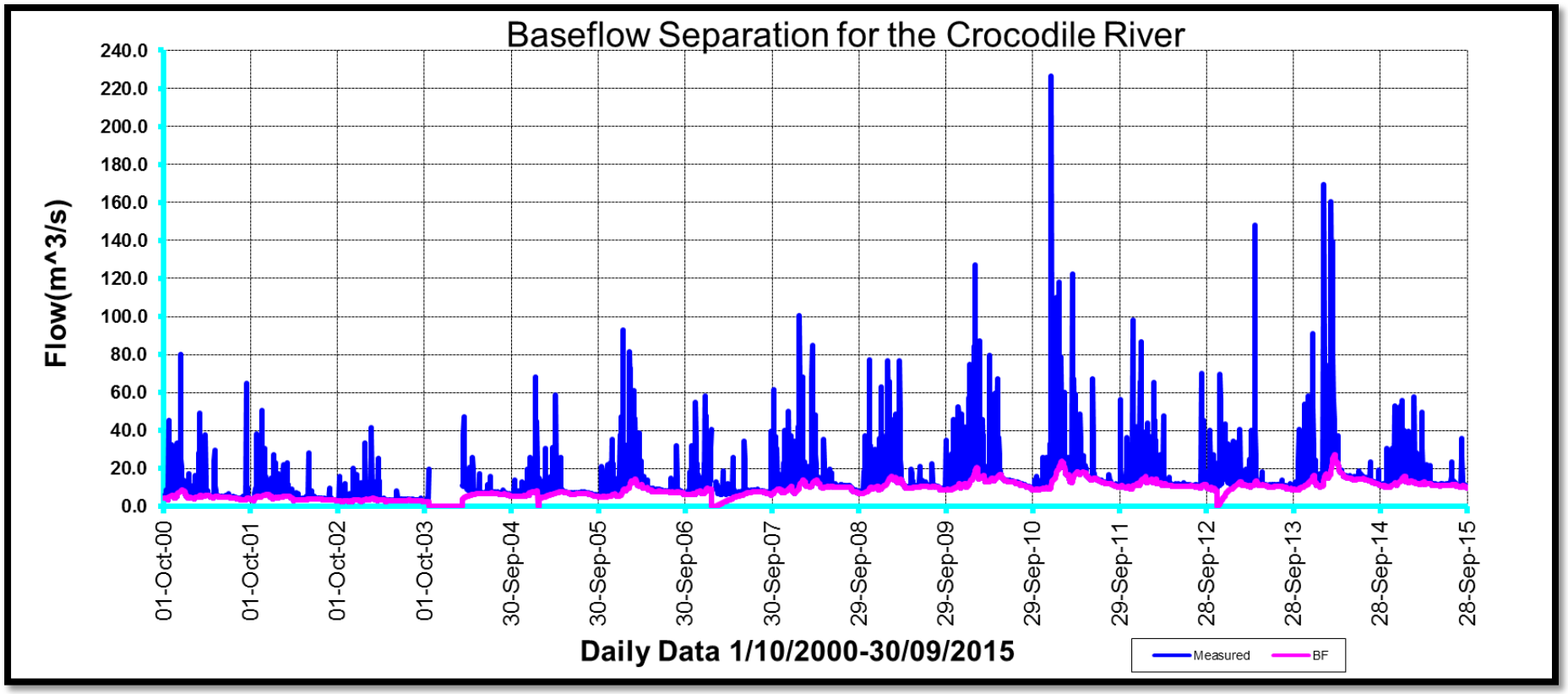

Figure 18: Graph of baseflow separation of the Crocodile River entering Hartbeespoort Dam from 1/10/2000 to 30/09/2016.

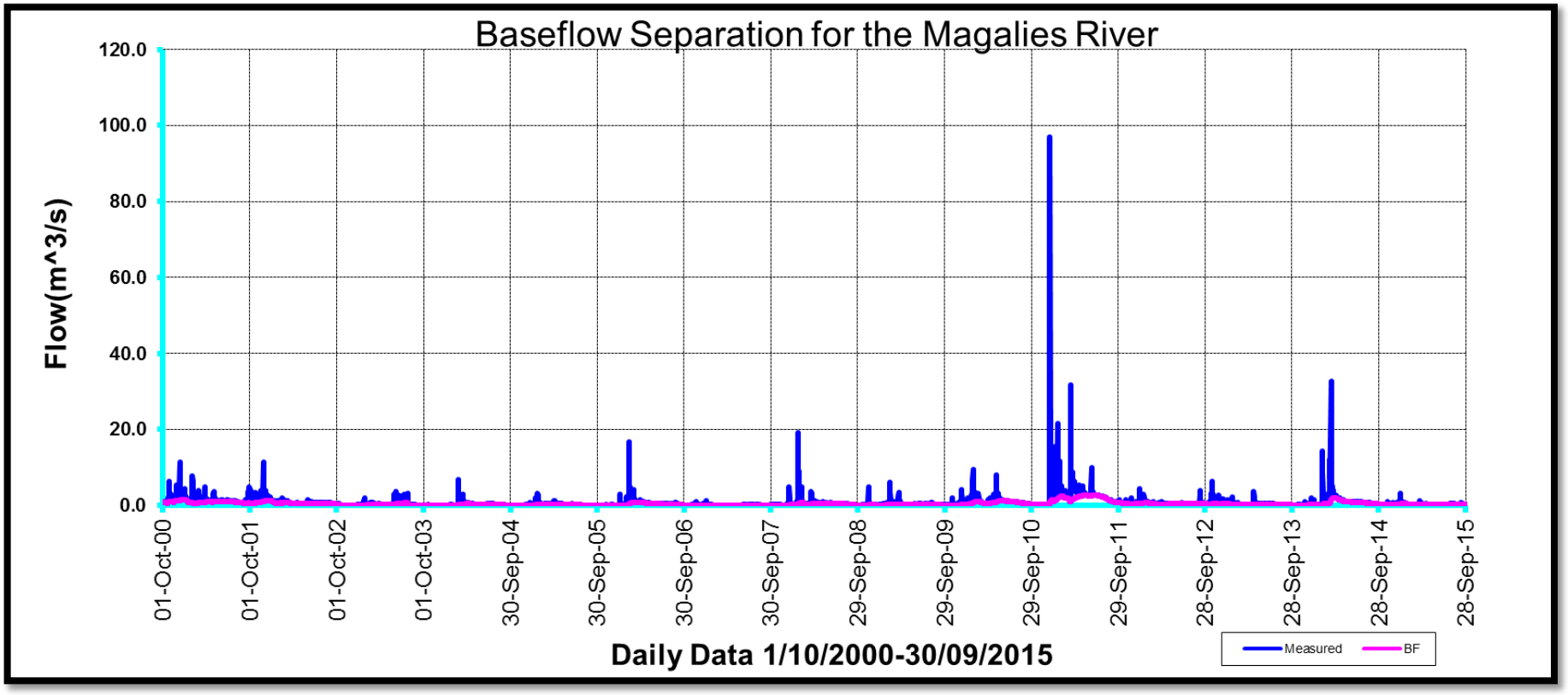

Figure 19: Graph showing baseflow separation of Magalies River from 1/10/2000 to the 30/09/2015.

The baseflow separation was taken for two of the rivers that contribute the majority of water into the dam; the Crocodile River and the Magalies River. The Swartspruit was ignored because it only contributes 0.3% of all the water in the dam. A one parameter recursive digital filter for baseflow separation was used because the flow data was daily and not monthly. The attenuation was used at 0.995 because it was found to be ideal for South Africa by Hughes et al. (2003).

The data indicated a jump in values of the Crocodile River baseflow post 2005 which mimicked that of the groundwater change. This was more than double the amount. The missing data in 2004 would not have made a large enough difference to account for the jump from 2005 hence it must have been the influence and addition of sewage. In order to reach a correct estimate of baseflow, the sewage was subtracted and an average value for baseflow from the Crocodile River entering the dam was estimated.

The Magalies River baseflow was also calculated and contributed approximately 12% of the total baseflow which correlates well to the 9% seen in 2008 (Roux & Oelofse, 2010).

4.7 Groundwater Loss Calculation

The groundwater leaving the Hartbeespoort Dam through the ground was calculated at 14Mm^3 on average per year over the past 15 years as seen in Table 13.

Table 13: Average groundwater leaving the Hartbeespoort Dam.

Crocodile G_{in} m^3	Magalies G_{in} m^3	ΔG m^3	G_{out} m^3
17 727 320	14 790 384	18 345 472	14 172 232

This value represents the amount of water exiting the dam through the ground or dam wall and thus the dam is recharging the groundwater.

The 14Mm^3 water exiting the dam needs to be accounted for. The addition of sewage from the Magalies River would increase this amount. The life of a dam wall is approximately 22 years before improvements are needed (International Atomic Energy Agency, 2017). Thus this value could be partly due to a loss of water through leaks in the dam wall. However, this

would not account for all of 14Mm^3 loss of water. Tracer dyes can be used to check for leaks in the dam wall and to see where the water is leaking to. Loss of water through the faults could also account for the high amount of water loss. Another source of loss is through the geology under the dam. The quartzite would however make this unlikely due to its impermeable nature. Water escaping through the embankments of the dam is another likely cause due to the permeable shale layering. This could explain the sample 26 which shared isotopic signatures with the dam water.

4.8 Possible Sources of Uncertainty

Uncertainty in the tritium results could be the differences in rainfall as an input function. The Magalies River sample would have a different input function from that of the Crocodile River sample due to the spatial separation of the recharge zones. A better estimate would be a rain sample for long term data near the recharge area of the Magalies River.

The variation in area with storage capacity is a good way to estimate area but it is still not 100% accurate. An acceptable error of 0.4% underestimation of the generated abstraction data was calculated. The change in groundwater was estimated to have an acceptable error of 3.9%.

The baseflow separation method contained a few days of missing data but this would not have affected the results of 15 years' worth of daily data to a large enough extent.

The decision to exclude the Swartrivier from the study may have contributed to added uncertainty to both the water balance and baseflow separation but since the contribution of inflow is 0.3%, from data taken from 1990 to 2008, of the total it can be considered a small variation (Roux & Oelofse, 2010). The sewage volume not included for the Magalies River due to unavailability data could also alter the baseflow separation significantly. Since the Magalies River contributes only 9.3% of the total flow, the alteration of the values could alter the values by approximately 10% but since it is within 3% of the actual value it should have little affect (Roux & Oelofse, 2010). The variation of sewage input, over the 15 year period, was not taken into consideration and affects the values calculated by the baseflow separation.

The groundwater calculation for the water exiting the dam made an assumption that the water entering the dam through the fault was equal to the water exiting the dam through the fault. This process can be improved by using transmissivity of the faults entering and exiting the dam but it was beyond the scope of this research. The values taken from upstream mining

areas could have been used but this would have been located in a different geology from that at the dam. Book values for lithology could have been used but this would not have accounted for the influence of the structures.

Chapter 5 Conclusion

Hartbeespoort Dam is an important source of water for the agricultural community as well as the public who have been using it as potable water since the turn of the 20th century. The establishment of the dam was to aid the community during times of drought. The possible threat to this resource can impact the people of semi-arid South Africa negatively.

The stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ indicated that the groundwater and the surface water were separated in winter. Samples from the summer samples showed recent rain isotopic signatures. The tritium results when compared to $\delta^{18}O$ showed two distinct sources for the summer samples. The Magalies River and Crocodile River samples showed two distinct sources. The Magalies River sample resembled the groundwater while the Crocodile River sample was mixed with sewage input which would share isotopic signatures from a different source. The spatial mapping revealed that the metals are gathering at the dam wall, settling and accumulating in the sediment. The tritium map indicated that the source of contamination was near a local nuclear power station called Pelindaba and was entering via the Crocodile River from runoff as well as return flow from agriculture. The spring and borehole near the dam, along the normal fault, also showed signs of contamination. This indicates that caution should be taken when establishing any reservoirs for potable water near the dam as boreholes and springs could be contaminated by metals as well as tritium.

The dam water balance was successfully established for a 15 year period and revealed that the groundwater gain was greater than the groundwater lost by the dam by 18 345 472m^3. This gain was attributed to the agricultural return flow as well as the increase in sewage. The seasonal variation showed that the stress on groundwater was increased in the dry months due to agricultural factors. Over the 15 year study period, a steady increase in the loss decreased the change in groundwater by of 10Mm^3.

The amount of baseflow entering the dam underneath the rivers was 32 517 704 m^3 and the water exiting the dam was 14 172 232m^3. The former value can be improved in the future when the values for sewage of the Magalies River are available for long term data. The latter needs further investigation using a tracer method to check possible leakages through the dam wall, geophysical studies on the nature of water flow in the Brits Graben at Hartbeespoort dam and also further environmental isotopic studies in different lithologies around the dam to ascertain seepage paths.

This research, certainly, highlighted some areas that threaten the Hartbeespoort Dam water as a resource. The accumulation of heavy metals and tritium may well cause problems for the agricultural industry and consequently for South-Africans who rely on it for domestic, industrial, agricultural and mining. The use of borehole water, although not mixed with the contaminated water in some cases, could be a risk, and as such, caution and testing should be done in order to understand, not just the quality of the water, but also the hydrogeological processes that may impact it in the future.

Although storage of water in the dam remains relatively constant throughout the year there seems to be an increasing loss of water from the dam to the ground. This suggests that great pressure is being put on the underlying aquifer. This loss was attributed to the increasing stresses put on the resource by agricultural pumping as well as the increase in mining activity. The loss has also increased the amount of water escaping from the dam by 10 000 000 m^3 over the last 15 years. How much of this increased pressure the aquifer beneath the dam can handle before it is depleted is a question for further exploration.

References

Abiye, T.A., Mengistu, H., Masindi, K. & Demile, M. 2015. SURFACE WATER AND GROUNDWATER INTERACTION IN THE UPPER CROCODILE RIVER BASIN , JOHANNESBURG , SOUTH AFRICA : ENVIRONMENTAL ISOTOPE APPROACH. *South African Journal of Geology*. 118.2:109–118. DOI: 10.2113/gssajg.118.2.109.

Ashton, P.J., Moor, F.C. De, Chutter, F.M., Cochrane, K.L., Jarvis, A.C., Robarts, R.D., Scott, W.E., Thornton, J.A., et al. 1985. *The Limnology of Hartbeespoort Dam*.

Bean, J., Beekman, H.E., Braune, E., Bredenkamp, D.B., Cave, L., Hughes, G.O., Lerner, D.N., Lorentz, S.A., et al. 2003. *Groundwater Recharge Estimation in Southern Africa Edited by Printed in Cape Town*. Y. Xu & H.E. Beekman, Eds. Cape Town: UNESCO Paris.

Botha, T.L. 2012. A histology-based fish health assessment to determine the health and reproductive status of Clarias gariepinus in the Hartbeespoort Dam , South Africa. University of Johannesburg.

Bradl, H. 2005. *Heavy metals in the environment*. H. Bradl, Ed. Neubrucke: Elsiever Academic Press.

Cawthorn, R.G. & Webb, S.J. 2001. Connectivity between the western and eastern limbs of the Bushveld Complex. *Tectonophysics*. 330:195–209.

Cheney, E.S. & Twist, D. 1991. The conformable emplacement of the Bushveld mafic rocks along a regional unconformity in the Transvaal succession of South Africa. *Precambrian Research*. 52:115–132.

Chutter, F. & Rossouw, J. 1991. *The managemen of phosphate concentrations and algae in Hartbeespoort Dam*.

de Clerc, M. 2010. Ecohydraulic modelling of the Crocodile River and the Hartbeespoort Dam. Gent University.

Coetzee, P.P. 1993. Determination and Speciation of Heavy Metals in Sediments of the Hartbeespoort Dam by Sequential Chemical Extraction. *Water SA*. 19(4):291–300.

Department of water affairs. 1996b. *WATER QUALITY GUIDELINES AGRICULTURAL USE : IRRIGATION*.

Department of water affairs. 2009. *Hartbeespoort Dam R e s o u r c e M a n a g e m e n t P l a n , 1 Edition*.

DH Environmentals. 2004. *Hartbeespoort Dam Remediation Project (Phase 1)*.

Dube, Z.A. 2010. The Merensky Reef and UG2 layers at De Wildt , western limb of the Bushveld Complex.

Eales, H.V. & Cawthorn, R.G. 1996. The Bushveld Complex. In *Layered Intrusions*. R.G. Cawthorn, Ed. Elsevier Science. 181–229.

European Commission. 2015. *Guidance Document No.34. Guidance document on the application of water balances for supporting the implementation of the WFD*. Luxemborg. DOI: 10.2779/352735.

Ginkel, C.E. Van, Hohls, B.C. & Vermaak, E. 2001. A Ceratium hirundinella (O . F . Müller) bloom in Hartbeespoort Dam , South Africa. *Water SA*. 27(2):269–276.

Harding, B. 2004. 6 water quality & reservoir management. *Water Wheel*. (November/December):6–10.

Harmon, R.S., Dugan, J.P., Borthwick, J., Harmon, R.S., Gagnier, M.A., Glahn, J.E., Kinsel, E.P., Macleod, S., et al. 1985. Guanidine hydrochloride method for determination of water oxygen isotope ratios and the oxygen-18 fractionation between... *Analytical Chemistry*. 57:1734–1736. DOI: 10.1021/ac00285a051.

Hughes, D.A., Hannart, P. & Watkins, D. 2003. Continuous baseflow separation from time series of daily and monthly streamflow data. *Water SA*. 29(1):43–48. Available: http://www.wrc.org.za.

IAEA. 1992. *Statistical treatment of data on environmental isotopes in precipitation*. Vienna. Available: http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Statistical+Treatment+of+Data+on+Environmental+Isotopes+in+Precipitation#0.

IAEA/WMO. 2016. *The Global Network of Isotopes in Precipitation*. Available: http://www.iaea.org/water.

International Atomic Energy Agency. 2017. *Investigating leaks in Dams & Reservoirs*.

Vienna. Available: https://www.iaea.org/technicalcooperation/documents/sheet20dr.pdf.

Kumambala, P.G. & Ervine, A. 2010. Water Balance Model of Lake Malawi and its Sensitivity to Climate Change. *The Open Hydrology Journal*. 4:152–162.

Labaugh, J.W., Schuster, P.F., Reddy, M.M. & Aiken, G.R. 1997. Hydrological and Chemical Estimates of the Water Balance of a Closed-Basin Lake in North Central Minnesota. *Water Resources Research*. 33(12):2799–2812.

Leyland, R.C. 2008. Vulnerability mapping in Karst terrains , exemplified in the wider Cradle of Humankind World Heritage Site . University of Pretoria.

McCarthy, T. & Rubridge, B. 2005. Basins on the Early Continent. In *The Story of Earth & Life*. 1st ed. R. Reid, Ed. Cape Town: Struik Nature. 94–145.

Moriarty, P., Batchelor, C., Abd-Alhadi, F.T., Laban, P. & Fahmy, H. 2007. *The EMPOWERS Approach to Water Governance: Guidelines, Methods and Tools*. INWRDAM. Available: http://empowers.info/page/2850.

Nkosi, S.C. 2016. Application of fate and transport models to evaluate the efficiency of a Cr (VI) remediation pump and treat system. University of Witwatersrand.

Perlman, H. 2017. *Water properties: Dissolved oxygen*. Available: https://water.usgs.gov/edu/dissolvedoxygen.html.

Phillips, F.. M. & Castro, M.C. 2014. Groundwater Dating and Residence-Time Measurements. In *Treatise on Geochemistry*. 2nd ed. V. 7. Elsevier Ltd. 361–400. DOI: 10.1016/B978-0-08-095975-7.00513-1.

Reta, G.L. 2011. GROUNDWATER AND LAKE WATER BALANCE OF LAKE NAIVASHA USING 3-D TRANSIENT GROUNDWATER MODEL BALANCE OF LAKE NAIVASHA USING 3-D TRANSIENT GROUNDWATER MODEL. University of Twente.

Robarts, R.D., Ashton, P.J., Thornton, J.A., Taussig, H.J. & Sephton, L.M. 1982. Overturn in a hypertrophic , South Africa) warm , monomictic impoundment (Hartbeespoort Dam ,. *Hydrobiologia*. 97:209–224.

Roux, S.P. & Oelofse, S.H.H. 2010. *THE RISING COSTS OF BOTH SEWAGE TREATMENT AND THE PRODUCTION OF POTABLE WATER ASSOCIATED WITH*

CROCODILE-WEST MARICO WATER MANAGEMENT AREA (A CASE STUDY). Pretoria.

SaExplore. 2014. *Hartbeespoort Climate*. Available: http://saexplorer.co.za/south-africa/climate/hartbeespoort_climate.asp.

Thornton, J.A., Mcmillan, P.H. & Romanovsky, P. 1989. Perceptions of water pollution in South Africa : Case studies from two water bodies (Hartbeespoort Dam and Zandvlei). *South African Journal of Psychology*. 19(4):199–204.

Toerien, D. & Walmsley, R. 1978. The Dissolved Mineral Composition of the Water Flowing into and out of the Hartbeespoort Dam. *Water SA*. 4(1):25–38.

Venter, P. 2004. 16 eutrophication management. *Water Wheel*. (January/February).

Vining, K.C. & Vecchia, A. V. 2007. *Water-Balance Simulations of Runoff and Reservoir Storage for the Upper Helmand Watershed and Kajakai Reservoir, Central Afghanistan*. Virginia. Available: http://pubs.usgs.gov/sir/2007/5148/.

Vorster, P. 1985. A Water Balance Forecast Model for Mono Lake, California. California State University.

West, A.G., February, E.C. & Bowen, G.J. 2014. Spatial analysis of hydrogen and oxygen stable isotopes (" isoscapes ") in ground water and tap water across South Africa. *Journal of Geochemical Exploration*. 145:213–222. DOI: 10.1016/j.gexplo.2014.06.009.

Wittmann, G. & Forstner, U. 1975. Metal Enrichmen of Sediments in Inland Waters- The Hartbeespoort Dam. *Water SA*. 1(2):76–82.

WRC. 2012. *Dam Abstraction*. Available: http://waterresourceswr2012.co.za/resource-centre/ [2017, February 01].

Appendix A-F: Refer to CD